REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 1998	3. REPORT TYPE AND DATES COVERED Final 1 Feb 1995 – 30 Sept 1996

4. TITLE AND SUBTITLE
Surface Treatment of High Performance Marine Alloys to Enhance Crevice Corrosion Resistance in Critical Seawater Applications

5. FUNDING NUMBERS
C
N000144-95C-001

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, Virginia 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
N/A

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

DTIC QUALITY INSPECTED 2

13. ABSTRACT (Maximum 200 words)

Electropolishing and applied cerium surface treatments to enhance the crevice corrosion resistance of high performance marine alloys used for critical seawater applications have been investigated. Because of its known susceptibility to crevice corrosion under certain adverse geometrical conditions, Ni-base alloy UNS N06625 was selected as the test material. Crevice corrosion tests were performed in natural and chlorinated seawater over a wide range of ambient temperatures for up to 180 days. Testing comprised the use of two different crevice conditions which previously contributed to crevice corrosion of the test alloys in the as-produced condition. Flowing seawater tests results were complemented by the results of electrochemical tests and SEM/EDS analysis. While both surface treatments markedly improved crevice corrosion resistance, electropolishing provided the greatest improvement in the seawater tests and enhanced performance during anodic potentiodynamic polarization testing in a low pH simulated crevice solution. The role of surface chromium depletion in the as-produced material is discussed.

14. SUBJECT TERMS
crevice corrosion, electropolishing, nickel-based alloy, cerium treatment, seawater, chlorination

15. NUMBER OF PAGES
78

16. PRICE CODE
N/A

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

SURFACE TREATMENT OF HIGH PERFORMANCE MARINE ALLOYS TO ENHANCE CREVICE CORROSION RESISTANCE IN CRITICAL SEAWATER APPLICATIONS

**Final Report on the Benefits and
Limitations of Electropolishing and
Cerium Surface Treatments
Contract No. N000144-95C-001**

Prepared for

Office of Naval Research
Arlington, VA

19980126 099

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January 1998

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ABSTRACT

Improved resistance of nickel-based alloy UNS N06625 to crevice corrosion in natural and chlorinated seawater has been demonstrated by the use of two different surface enhancement techniques. The most successful technique employed commercial electropolishing. While surface treatment with cerium was shown to be beneficial, the resistance imparted was not as great as that afforded by electropolishing. The results of long term crevice corrosion testing, supported by electrochemical testing and SEM/EDS surface analyses are discussed. This work was developed in response to US Navy interest as expressed in SBIR-RFP No. 93-051. The program was funded by the Office of Naval Research under contract No. N000144-95C-001.

INTRODUCTION

Nickel-base alloy 625 (UNS N06625) is considered to be a highly corrosion resistant alloy and is commonly included in lists of "high performance marine materials." However, N06625 is known to be susceptible to crevice corrosion in both natural and chlorinated seawater.[1-9] The susceptibility to attack appears to be highly dependent on crevice geometry, as well as other factor.[5-11] Most of the crevice corrosion reported for N06625 has been associated with conditions produced by non-metallic crevice formers, but attack at all metal sites is also possible. In 1989, Klein et al., summarized a number of conditions and crevice forming materials which lead to attack of N06625 in laboratory and seawater field tests.[5] While some of the test

geometries were contrived as a matter of convenience for testing purposes, others were more closely related to practical engineering applications, but not necessarily exact "mock-ups", or accurate simulations of particular service conditions. Additional seawater testing, electrochemical studies and mathematical modeling of N06625 have since been reported.[6-9,11]

Traditionally, two approaches to crevice corrosion prevention have been taken; the first is to use more highly alloyed materials, i.e. those with higher levels of Cr, Mo and N, and the second is to employ sacrificial cathodic protection. The elimination of crevices, per se, is not always possible or desirable. In response to US Navy interest in crevice corrosion countermeasures expressed in SBIR-RFP No 93-051, LaQue Corrosion Services, with technical support from McMaster University, Hamilton, Ontario, Canada proposed to demonstrate the efficacy of two different surface modification techniques as applied to the subject alloy N06625. This report describes research into the benefits of electropolishing and cerium surface treatments for critical application involving N06625 in natural and chlorinated seawater. As will be described, the parametric study included replicate testing to assess the countermeasures when subjected to variations in crevice geometry, seawater temperature and test duration. These tests were subsequently complemented by electrochemical testing and surface chemistry analyses.

Electropolishing

Electropolishing has long been viewed as a technique to enhance to corrosion resistance of stainless steels. Relatively recent studies, for example, have shown that the crevice corrosion propagation resistance of Type 316 stainless steel (UNS

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S31600) in natural seawater was improved by electropolishing.[12,13] The benefit in artificial seawater and other (lower) chloride-containing waters was observed to be even greater.[12] In another series of tests aimed at identifying candidate reverse osmosis pressure vessel materials, electropolished Type 316L (UNS S31603) tubing exhibited better performance than as-produced tubing of a 6% molybdenum-nitrogen containing stainless steel in a 90-day seawater test.[13]

Electrochemical studies performed on electropolished S31600 have indicated greater "stability" of the passive film in simulated crevice solutions and revealed marked changes in the cathodic polarization behavior in natural seawater and other chloride-containing waters, compared with as-produced and ground material.[12] Additionally, electropolished stainless steel appeared to be less affected by biofilm ennoblement than non-electropolished material.[12]

Cerium Treatment

Propagation of crevice corrosion is dependent on conditions inside and outside the crevice, i.e., differential oxygenation. The cathodic half-reaction, which drives the corrosion cell, occurs outside the crevice. Research at McMaster has demonstrated that an alternative means of enhancing the crevice corrosion resistance of stainless steels is to "inhibit" the cathodic reaction. This extension of an earlier study[14] on the kinetics of cathodic processes (hydrogen and /or oxygen reduction) in chloride solutions indicated a dramatic "inhibition" of the cathodic reactions when stainless steels were ion-implanted with cerium.

Ultimately, the ion-implantation approach was replaced by a "chemical conversion" treatment process that is more viable from a potential commercial production standpoint. The latter was shown to be effective in improving the crevice corrosion resistance of a range of austenitic stainless steels, both in the ASTM G48 ferric chloride test (method B), and other tests comprising exposures to natural seawater, with and without chlorination.[15] Further development to optimize the chemistry and the physical conditions of the treatment process was undertaken at McMaster University in preparation for the subject investigation.

EXPERIMENTAL

Materials and Specimens

All test specimens were prepared from one length of 1-in schedule 40, INCONEL® alloy 625 pipe having the heat chemistry shown in Table 1. Figure 1 provides photomicrographs (100X and 1000X magnification) showing the etched microstructure of the as-produced (cold rolled pickled and annealed) pipe. A total of 100 specimens were cut and end-machined to a final length of 100 mm (4 in). Each specimen was engraved with an alphanumeric code (in this case NO3AV) indicative of the alloy and heat identification, followed by sequential numbering 001 to 100. As indicated in Table 2, the first 20 specimens (001 to 020) were retained as untreated controls. Specimens 021 to 060 were sent to a vendor (ABLE® Electropolishing Company, Chicago, IL) for electropolishing. Fifty percent of these received electropolishing on both the ID and OD surfaces of the pipes, and the remainder on the OD only. Non-proprietary details of the electropolishing procedure are given in Appendix 1. Specimens numbered 061 to 100 were sent to McMaster

University for surface treatment with cerium. Those identified 061 to 080 were processed with McMaster's Materials Laboratory's cerium A treatment, and those identified 081 to 100 were processed with their modified cerium B treatment. The cerium A treatment was performed in a solution very close to that used originally to treat stainless steel.[15] The solution used in the cerium B treatment also contained lanthanum and gadolinium.

Crevice Formers

Two types of crevice formers were utilized in these investigations: vinyl sleeves and rubber gland type compression fittings. Both types have been previously used in other crevice corrosion tests conducted for alloy NO6625, as well as other investigations involving nickel-base and stainless type alloys.[5,13] Vinyl sleeves were prepared by cutting sections of TYGON® tubing (formulation R 3603) having nominal dimensions of 1¼ in (31.8 mm) ID x ¼ in (6.4 mm) wall. For the six originally scheduled tests, the sleeves were cut to nominally 64 mm (2½") lengths. As will be discussed, an additional test comprising sleeves cut to approximately 76 mm (3") was also conducted. Prior to use, the sleeves were ultrasonically cleaned with a commercial laboratory glassware detergent, rinsed with tap water and dried. Figure 2 shows the completed assembly of pipe specimens fitted with vinyl sleeves. In each case, the sleeves covered approximately 25.4 mm (1 in.) of the specimen at both ends. In as much as the OD dimension of the pipe was greater than the ID of the vinyl sleeve, a tight interference fit was created. Serrated nylon hose clamps secured the sleeves. The clamps were approximately 8 mm (5/16 in), in width and were positioned at a distance of about 6.4 mm (¼ in) from the ends of the pipe. The clamps were first finger tightened and then further tightened with pliers. Consis-

tency in tightening was attempted by counting the number of "clicks" created by the advancing serrations.

Figure 3 shows an "exploded" view of the compression fittings. Whereas all of the tests included specimens with vinyl sleeves, compression fittings were utilized only in the 180-day tests. Each of the two rubber glands contained within the PVC fittings were 18 mm (~0.7 in.) in width, and had a pre-compression ID of about 33.5 mm (1.32 in). Since the compression fittings were off-the-shelf hardware, no pre-cleaning treatment of the glands was performed. Figure 4 shows a typical completed assembly. Consistency in tightening was achieved, to the degree possible, by screwing the compression caps down the full length of the threads on the bodies of the fittings.

Test Loops

Once-through seawater test loops were prepared by connecting the series of specimens end-to-end with the previously described crevice formers. Inlet and outlet end plumbing was constructed of PVC piping. Figure 5 shows a typical test loop. Sixty-day test loops comprised duplicate specimens with vinyl sleeves (total 10 specimens) and the 180-day tests comprised duplicates as above, and also with compression fittings (total 20 specimens).

Seawater Supply

Seawater was pumped directly from Banks Channel into two polyethylene head tanks. The supply of seawater was continuous and allowed to overflow through a drain provided. Seawater was drawn from near the bottom of the tanks,

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and pumped through the test loops. A calibrated rotameter, located upstream of the specimens, enabled control of the bulk flow at 8.5 gpm (±0.5 gpm), which equated to a nominal seawater velocity of 1 m/s (~3 fps) through the pipe specimens. The seawater flow was checked and adjusted as necessary 9 times daily (3 times per 8-hour shift).

Photographs in Figure 6 provide overall views of the supporting apparatus. For those tests requiring chlorination, an auxiliary tank to hold liquid sodium hypochlorite (bleach) and a metering pump was placed in line for direct feed into one of the two seawater tanks.

Environmental Conditions

Table 3 gives the weekly routine hydrology for the untreated source seawater. One of the objectives of these investigations was to determine any effect of seawater temperature and associated seasonal biofouling on the performance of NO6625 with and without surface enhancement. Seawater temperature data for the various tests that commenced at different times of the year are provided in Table 2. The identification of the various specimens exposed in each test is also provided in Table 2.

As indicated, two series of tests involving chlorinated seawater were conducted; an 180-day test commencing in the spring when the seawater temperature at the start was 19.8°C, and a 60 day test commencing in the summer at a temperature of 25.0°C. Colorimetric Diethyl-p-Phenylene-Diamine analyses for free available chlorine (FAC) were performed a minimum of 6 times daily. These were coordi-

nated with various levels of rising and falling tides. Figures 7 and 8 provide distribution plots of the FAC analyses performed during the 180-day and 60-day tests, respectively. During the longer test, over 80 percent of the FAC analyses were within the 0.5 ± 0.2 mg/ℓ target range. Another 14 percent of the analyses either exceeded or were below the target range by 0.1 to 0.2 mg/ℓ FAC. Six percent of all analyses were somewhat higher, but only one measurement exceeded 1.0 mg/ℓ. Fluctuations in FAC are clearly related to variations in the temperature and biological activity in natural seawater. FAC levels were controlled by adjusting the feed and stroke settings on the metering pump, followed by reanalysis after some period of time, usually within 15 minutes.

Electrochemical Studies

Cyclic potentiodynamic polarization curves were developed while exposing pipe OD surfaces to a nitrogen deaerated, simulated crevice solution. Cathodic potentiodynamic sweeps were performed on pipe ID surfaces exposed to natural seawater. Details are provided in the Results section.

RESULTS AND DISCUSSION

Overall Resistance to Crevice Corrosion Initiation

Of the 200 crevice sites present an the various N06625 pipe specimens exposed in this investigation, 73 percent remained resistant. Table 4 summarizes the overall incidence of attack incurred (1st column), as well as that associated with the different crevice formers and seawater conditions. As indicated, the as-produced pipe specimens were found to be the most susceptible and the electropolished ones

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the most resistant. In the case of electropolished material, crevice corrosion was limited to a small area of superficial corrosion at a single rubber gland site in one of the chlorinated seawater exposures. Crevice corrosion resistance exhibited by the cerium treated material was markedly improved over that for the as-produced material, but substantially less than that exhibited by the electropolished materials. Overall, the resistance of the cerium A treated and cerium B treated material were comparable to each other. Based on the percent of sites attacked, data in Table 4, there was a greater incidence of attack for pipes tested with the rubber gland type compression fittings than those exposed with vinyl sleeves, thus refuting notions that the crevices formed by vinyl sleeve assemblies, as used in present and previous tests[5], were overly severe.

In-situ Inspections

The translucent nature of the vinyl sleeve materials facilitates *in-situ* inspections, which can provide information concerning the approximate time to crevice corrosion initiation, and can also be used to monitor lateral propagation of attack. Examples of the latter are provided in the series of photographs shown in Figure 9. Such inspection was not possible for the specimen tested with the opaque PVC compression fittings.

Table 5 provides a summary of the earliest crevice corrosion detection times for the vinyl sleeve fitted specimens. The numbers following the hyphen in the specimen code indicates the number of days tested. In some cases, the actual location of the affected crevice area may have hindered its detection sooner. As indi-

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cated, a number of affected sites went undetected. The earliest detection time is shown for sites on the as-produced material in the chlorinated seawater tests.

Crevice Corrosion Propagation Results

Tables 6 to 11 identify those pipe specimens found to be susceptible and provide propagation data for the affected crevice sites. Percent affected area data were obtained by placing a transparent grid over the crevice site and counting the number of 1 mm^2 divisions defining the attack. Depth of penetration measurements were obtained with a needle point dial depth gage in the manner described elsewhere.[7,8]

60-Day Tests with Vinyl Sleeves

Table 6 compares the resistance of the various test pipes assembled with vinyl sleeves and exposed to warm natural (NSW) and chlorinated (CSW) seawater for 60 days. As indicated, crevice corrosion affected at least one site on each of the as-produced pipes. The greatest attack, comprising both area and depth, was found in the untreated seawater test. While some variability in the affected area data is shown by the chlorinated seawater test results, the maximum depth of attack was consistently low (<0.01 mm) from site to site. Figure 10 shows post-test views of two representative specimens. All sites on the cerium treated (A and B) and electropolished pipes were resistant during the 60 day exposure to chlorinated seawater. While cerium A and electropolished pipes were also fully resistant to untreated seawater, one of the four available crevice sites on the two cerium B treated pipes incurred some attack. However, the affected area and depth of penetration was less than that incurred by as-produced pipe specimens.

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Effect of Test Duration - Warm Natural Seawater

Table 7 provides additional vinyl sleeve test results. In this case, results of the preceding 60-day test in warm natural seawater (Table 6) are compared with those for corresponding specimens which were exposed for an additional 120 days. As can be seen, all crevice sites on the electropolished specimens remained resistant for the full 180 days. For the other materials tested, results in Table 7 show an increase in the number of affected sites with increased test duration. However, as indicated in Table 4, some had initiated within the initial 60 day period. Significantly, the extended test duration did not promote any increase in the depth of penetration. Moreover, had the removal schedule for the as-produced specimens in Table 7 been reversed, an erroneous conclusion regarding propagation behavior may have been forthcoming.

Effect of Test Duration - Cold Natural Seawater

Table 8 gives results for as-produced and surface treated pipe specimens which had been fitted with vinyl sleeves and exposed to cold natural seawater. As indicated, all cerium (A and B) treated and electropolished specimens were fully resistant after 60 days' and 180 days' exposure. While the as-produced pipe was again found to be susceptible, the number of sites affected and the maximum areas of attack were somewhat less than shown previously in Table 7 for the warm seawater tests. As can be seen, penetration at the three affected sites was minimal. Figure 11 provides in-situ views of the affected sites. Figure 12a provides a post-test view of the attack incurred in 180 days.

Effect of Seawater Temperature - Compression Fitting Tests

Table 9 compares results for specimens assembled with the rubber gland compression fittings and exposed to warm and cold natural seawater for 180 days. Under these conditions, only the electropolished specimens remained fully resistant. In terms of the numbers of sites affected in the respective tests, the cerium A and B treated material was more resistant than the as-produced material, but in some cases the affected areas were similar. In cold seawater there was no difference in the maximum depth of penetration at sites on the as-produced and cerium treated specimens. As shown in Table 9, the maximum depth of attack for the as-produced pipe exposed to warm seawater was 0.04 mm, which is about five times less than the maximum depth noted earlier for similar material exposed with vinyl sleeves for only 60 days. Figure 12b shows the appearance of one of the as-produced pipe specimens which had been exposed to cold seawater for 180 days.

Effect of Crevice Formers - 180-Day Chlorinated Seawater Tests

In addition to the in-situ views shown in Figure 9, several post-test views of affected specimens are shown in Figures 13 to 15. Table 10 compares the crevice corrosion behavior of specimens exposed with vinyl sleeves and rubber gland compression fittings in a 180 day chlorinated seawater test. In this case the seawater temperature was 19.8°C at test initiation, but increased with seasonally warmer temperatures. As can be seen, all eight crevice sites on the as-produced material incurred attack, but with minimal depth of propagation. In contrast, the electropolished specimens were resistant except for a small 2 mm^2 area of superficial attack beneath one of the rubber glands. Both the cerium A and cerium B treated material were more resistant than the as-produced controls.

Additional Vinyl Sleeve Testing

As described earlier, a separation of 12-13 mm (~1/2 inch) was maintained between specimens joined together with the vinyl sleeves. This spacing, which was also used is some other previously reported tests,[8] was intended to minimize bulging of the vinyl due to in-line pump pressure. Conceivably, such bulging could alter the gap at the mouth of the crevice formed between the vinyl and pipe specimens. In an earlier crevice corrosion testing of this type,[5,6] but with direct connection to a main seawater feeder line, a separation of about 25 mm (~1 in) was used and some sleeve bulging did occur. Whether or not this condition lessened IR restriction at the crevice mouth and contributed to the more extensive propagation noted earlier by Klein et al.,[5] remains uncertain. However, as reported by Oldfield, some widening of the gap dimension, in both warm and cold seawater should decrease crevice cor-rosion propagation for N06625.[8] On the chance that the previous test conditions[5] were more severe than those described for this surface effects investigation, addi-tional pipe specimens were exposed with the larger separation (Figure 2 bottom). These tests were again operated directly from a main seawater header and com-menced at a seawater temperature of 29.2°C. The test lasted for 60 days. Results in Table 11 show no susceptibility for electropolished or cerium (A and B) treated specimens assembled with the longer vinyl sleeves (VSb). However, all four sites on the as-produced specimens incurred attack. In contrast to results from tests with the shorter sleeves (VSa), the maximum depth of attack was an order of magnitude less than those utilizing the longer sleeves. Moreover, these penetrations were nearly two orders of magnitude less than those reported by Klein et al.,[5] for vinyl sleeve (type VSb) testing of N06625 from a different heat. Effects of heat chemistry have been discussed elsewhere.[7] Accordingly, the variation in crevice assembly

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design does not appear to be a factor regarding the differences in crevice corrosion propagation reported above.

Corrosion Potentials

The corrosion potential of each pipe specimen was measured one or more times during the course of testing. These measurements were performed with a high impedance digital voltmeter, with one lead connected to a Ag/AgCl/seawater reference electrode located in the corresponding head tank and with the other lead in temporary contact with the OD surface of the specimen.

The bar graph in Figure 16 shows the range of corrosion potentials measured for specimens representing the three groups of materials after 1,000 hours in the four indicated tests. These data include potentials for vinyl sleeve and compression fitting assembled specimens having scheduled removals after 60 and/or 180 days. In this analysis, data for the cerium treated (A and B) and the electropolished (OD and OD/ID) specimens have been consolidated, respectively. The potentials shown in Figure 16 (and later in Tables 12 and 13) are mixed potentials indicative of anodic and cathodic reactions taking place on the boldly exposed pipe ID surfaces, as well as those within the crevice on the pipe OD. Results show respectively narrower ranges of potentials for the electropolished and cerium treated specimens, as compared with the as-produced material. Generally, the least variation among materials is noted for the tests commencing in cold natural seawater. As-produced and cerium treated specimens exhibited their greatest variability in the chlorinated seawater test which commenced in early spring. The greatest variation in potential among elec-

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tropolished specimens is shown by the data collected in the cold natural seawater test.

Tables 12 and 13 list the final potentials for all specimens in the various 60-day and 180-day tests respectively. The underlined data correspond to previously identified specimens which exhibited one or two affected crevice sites. While the most active potentials are associated with specimens which exhibited attack, not all affected specimens exhibited active potentials. These results demonstrate that in the presence of severe crevice geometries and potential ennoblement associated with chlorination or freely formed biofilms, the electropolished material remained highly resistant to crevice corrosion. While this can also be said for a number of cerium treated specimens, their overall resistance was less than that exhibited by the electropolished ones.

Electrochemical Testing

Following the seawater testing described above, pipe specimens were sectioned to provide electrochemical test electrodes. These were obtained from the center of the originally non-crevice areas of the pipes. Following attachment of an electrical lead wire, the electrodes were masked with a 2-part epoxy coating to provide a nominal 1 cm^2 window on either the ID or OD surfaces of the section. To complement the previous crevice corrosion test conditions, electrodes with exposed ID's were subjected to cathodic polarization in natural seawater. Those with exposed OD's were subjected to anodic polarization in a deaerated simulated crevice electrolyte. This approach is consistent with earlier investigations dealing with UNS S31600[12] and N06625[11].

Cathodic Polarization

Prior to cathodic polarization at a scan rate of 0.17 mV/min., electrodes were pre-exposed to nominally quiescent seawater for approximately 12 days to allow for some bio-film formation to occur. One set of electrodes was pre-exposed at a time when the average daily seawater temperatures over 12 days was 19.6°C and another set at 24.0°C. Figures 17 to 19 show the cathodic polarization curves for electrodes prepared from as-produced, electropolished and cerium treated (A) pipes tested after the two pre-exposure periods. As can be seen, exposure to the warmer seawater with its presumably increased level of bio-activity resulted in increased cathodic current associated with enhanced oxygen reduction and/or some other reaction.[16] Previously, Shaw et al.,[11] reported a similar trend as a function of exposure period which was accompanied with changes in seawater temperatures. Figure 20 compares cathodic polarization curves for the various test materials after pre-exposure to the warmer seawater environment. Note that the curve for the electropolished material is shifted toward a lower potential-current density regime relative to that for the as produced and cerium treated materials. It is presently uncertain if the observed differences in polarization behavior after pre-exposure to seawater is due do differences in bio-film formation or to the presence of an enhanced passive oxide layer on the electropolished material, or to some combination of the two. The observed shift for electropolished alloy N06625 is not as great as that reported previously in similar type tests for S31600.[12]

Anodic Polarization Behavior

Previously, Shaw et al.,[11] also reported on the anodic polarization behavior of N06625 in crevice solutions within the pH range of -0.25 to -1.2. In the present in-

vestigation anodic polarization tests were conducted in a saturated sodium chloride, pH 0.2 solution prepared with HCl and H_2SO_4 (10:1 volume of conc. acid). For these tests, cyclic polarization curves were developed at a higher scan rate (1.7 mV/min.) in an attempt to identify a low current anodic region (LCR) during the reverse scan portion of the experiment. As described elsewhere, this procedure was previously used to successfully identify optimum potentials for anodic protection in sulfuric acid media.[17]

Figure 21 compares the forward (neg.-positive) scan portion of the curve developed for the four test materials. As can be seen the current densities associated, for example, with the anodic peak, and the overall passive potential region were the lowest for the electropolished material. Current densities for the cerium treated (A and B) material were also appreciably lower than those recorded for the as-produced material. It can also be seen that range of positive potentials was somewhat greater for the electropolished material.

Figure 22 compares the full, forward and reverse scan, polarization curves for the as-produced and electropolished pipe electrodes. For the as-produced material, the reverse scan currents approximated those of the forward scan. This behavior is contrasted by that for the electropolished material which showed much lower reverse scan currents which are indicative of a more stable and, hence, more protective passive oxide. While not shown, the reverse scan behavior for the cerium A and cerium B approximated that of their respective forward scans.

The reverse scan low current region shown in Figure 22 for the electropolished material approximates that of the corrosion potentials for electropolished N06625 pipe in the natural and chlorinated seawater as describes in Figure 16 and Tables 12 and 13. Thus, under freely corroding conditions, crevices capable of generating an anolyte pH of 0.2, and perhaps lower, would remain resistant, or corrode at an exceedingly low rate.

Surface Analyses

Samples of the as-produced and electropolished (ID/OD) test pipes were subjected to Scanning Electron Microscope/Energy Dispersive Spectroscope (SEM/EDS) analyses by the same equipment and profiling technique employed in the previously reported study by Oldfield.[9] Analyses of the OD pipe surfaces were also performed. Results of the profiling analyses for chromium are plotted in Figure 23 as a function of distance inward from the edge of the cross-sectioned material. As can be seen, the analyses show considerable chromium depletion at the OD edge of as-produced pipe, and some enrichment at the OD edge of the electropolished pipe. The degree of depletion shown in Figure 23 is considerably greater than that described earlier by Oldfield[9] for mill pickled sheet material of the same alloy. At a profile depth of about 15μm, and inward, the level of chromium analyzed for both the as-produced and electropolished pipes approximated, within 1%, the actual level shown for the mill heat analysis. The above depth of chromium depletion at the surface of the as-produced pipe appears consistent with the near surface feature shown in the 1000X optical photomicrograph in Figure 1b.

Table 14 compares the levels of Ni, Cr, Mo and Fe as reported by the mill heat analysis (Table 1) and that determined by the preceding EDS analyses of the as-produced and electropolished pipe at the center of the cross-section and on the OD surface.

Additional SEM/EDS analyses of other sections from the same pipes described above were performed in-house with different equipment. In this case the analyses included an atomic number, absorption, florescence (ZAF) correction. Table 15 gives results obtained at the center of the cross-sectioned as-produced pipe, and also at the OD surfaces of both the as-produced and electropolished pipes. Analyses of the OD surfaces of one of the cerium A , and cerium B treated pipes was performed in-house and are also included in Table 15. No profiling, such as that described above by Figure 24, was performed on cerium treated material.

From Table 14 it is observed that the EDS bulk analyses performed at the center of the cross-section of both the as-produced and the electropolished pipe specimens are nearly identical, but differ considerably from the actual mill heat analysis. One would expect that the values obtained by EDS and the mill heat analysis to be in better, but not absolute, agreement.

Results shown in Table 15 also indicate a disparity between the EDS analysis performed at the center of the cross-sectioned as-produced pipe and the mill heat analysis. In this case the EDS determined level of chromium was higher and the molybdenum lower than that shown in Table 14. Because of the strong influence of chromium and molybdenum on crevice corrosion some attempt was made to normal-

ize the differences in the EDS results obtained from different sources and that between EDS and the mill heat analysis. Simple averaging of the EDS data identified center (bulk) in Tables 14 and 15 yields chromium and molybdenum levels which closely approximate those in the mill heat analysis. Also it was determined that the same of Cr + Mo for the three sets of EDS analysis performed at the centers of the as-produced and electropolished pipe approximate the Cr + Mo level from the mill heat analysis.

In order to compare the surface analysis results determined from the two different EDS sources, adjustment factors based on the above differences between EDS results at the cross-sectioned centers (bulk) and the actual mill heat analysis were assumed. For the raw EDS data shown in Table 14 an adjustment factor of 1.5 percent was introduced to lower the molybdenum and raise the chromium. For the raw EDS data shown in Table 15 an adjustment factor of 1.9 percent was used to raise the molybdenum and lower the chromium. Adjusted values are shown in Table 16.

Crevice corrosion resistance is often reported as a function of a material's PREN (pitting resistance equivalent number); % Cr + 3.3 x % Mo is a common expression used to calculate PREN for stainless type materials which do not have intentional additions of nitrogen. Calculated PREN values based on adjusted EDS data are also included in Table 16.

Averaging the adjusted data in Table 16 provides calculated PRE values of 34.8 and 50.7 for the as-produced and electropolished materials, respectively. The

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average PRE for the electropolished material closely approximates the PRE based on the bulk alloy composition. The average surface PREN value (38.4) for the cerium (A & B) treated pipes was found to be only marginally greater than that of the as-produced material. This is consistent with the view that cerium treatment is likely to have only modified the metal surface layers much shallower than the depth of the EDS analysis. Whereas surface grinding reported by Oldfield,[9] resulted in removal of a depleted surface layer (low PREN) associated with mill production (pickling), current work has demonstrated the benefits of electropolishing. The relationship between enhanced surface chemistry and alloy performance in the previously discussed vinyl sleeve and compression fitting tests, and also in electrochemical tests is discussed below.

Influence on Crevice Corrosion Initiation

Figure 24 provides a plot showing the relationship between the calculated PREN values, from adjusted EDS data, and the total number of affected crevice sites in all natural and chlorinated seawater tests discussed earlier in this report. For this example, results for cerium A and cerium B treated material have been averaged, as were those for the two series of electropolished pipes. As can be seen, the propensity for crevice corrosion initiation decreased with an increase in the value of PREN, as would be expected for similar comparisons of alloys with different bulk analyses. While the greatest benefit was associated with electropolishing, the influence of the applied cerium treatments was also substantial. The enhanced resistance provided by both the cerium (A and B) treatments and electropolishing in terms of crevice corrosion initiation can be related to the resistance of the respective materials in aggressive crevice electrolytes. Figure 25, for example, shows a plot of the

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anodic peak current maximum (from Figure 21) as a function of the PREN values developed form adjusted surface EDS data. As can be seen, one to two orders of magnitude improvement in resistance over that for the as-produced material is shown for the cerium treated and electropolished material, respectively.

Other Observations

According to literature provided by the electropolisher, this process involves removal of less than 1 mil (~25 µm) of material; more typically about 0.4 mils (10 µm). By reference again to Figure 23 and Figure 1b, it is apparent that this was sufficient to remove the chromium depleted surface layer in the as-produced N06625 pipe tested. Figure 23 may also be useful in explaining the limited penetration (≤0.01 mm) which occurred at all the affected sites on the as-produced pipe specimens exposed to cold natural seawater and to chlorinated seawater. Conceivably, as the initial attack following breakdown of passivity deepened it was confronted by the increasingly more corrosion resistant composition. As illustrated previously by Figure 23, this more resistant composition begins, in this material, at a profile depth of about 4 µm (0.004 or <0.01 mm). The occurrence of substantial deeper attack at several affected sites in the warm seawater tests is not consistent with the above discussion regarding gradations in material resistance from the surface inwards. Because chromium is considered to be a major contributor to the fall in pH within the crevice,[10] exposure to the higher chromium containing material below the now-removed depleted layer may have contributed to the development of a more acidic crevice environment, and hence greater propagation. However, the existence of high levels of chromium at the surface of the resistant electropolished specimens was shown to provide greater resistance to the anolyte investigated. It is

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conceivable that small variations in the actual crevice gap dimension may have resulted in more favorable conditions for accelerated propagation, particularly in warm seawater as described previously by Oldfield.[9]

SUMMARY AND CONCLUSIONS

The efficacy of two different surface treatments for enhanced resistance of nickel-base alloy N06625 to crevice corrosion in natural seawater has been investigated. The benefits and limitation of cerium treatments devised by McMaster University and standard electropolishing practices were established by long term testing in natural and chlorinated seawater, and supported by electrochemical studies and SEM/EDS analyses. Testing was rigorous in that it comprised exposures to seasonal variations in seawater temperatures and employed two different types of crevice formers. Moreover, the tested material was shown to have substantial depletion of chromium at the surface. Crevice conditions were severe in that deep-tight geometries were obtained with two different elastomeric materials. A total of 100 specimens were tested and evaluated. The key findings of this investigation are as follows:

- Electropolished N06625 exposed with tight vinyl sleeve crevice formers and rubber gland type compression fittings were resistant to crevice corrosion in natural and chlorinated seawater exposures of 60 days and 180 days duration. Superficial attack was limited to a single 2 mm^2 area at one of the 40 crevice sites.

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- Cerium treated (both A and B processes) material was substantially more resistant than the tested as-produced material, but lacked the resistance exhibited by the electropolished material. It is conceivable that yet greater benefits of cerium treatment could be derived when applied to alloy N06625 having a surface chromium content more representative of the alloys' bulk composition.

- For enhanced resistance to crevice corrosion, only electropolishing of the crevice area was necessary. This was supported by electrochemical testing which demonstrated that electropolishing had significant impact on reducing the maximum peak current during anodic polarization in a simulated crevice solution. While cathodic currents during polarization of electropolished pipe ID surfaces in the bulk seawater environment were only marginally lower than for as-produced material, this inhibition may have also contributed to the observed resistance.

- EDS analyses revealed chromium surface depletion due to mill processing. The minimal amount of metal loss due to electropolishing restored the surface chemistry to levels commensurate with that of the bulk alloy composition. While some test data has supported a beneficial effect of surface grinding to remove the depleted surface layer,[9] other test results have shown susceptibility for N06625 in the surface ground condition.[4]

- Comparisons of material performance with adjusted EDS results from surface analysis equated as PREN values (%Cr + 3.3 x %Mo) provided good correlation with electrochemical and immersion test results.

- Improved resistance to crevice corrosion for N06625 associated with electro-polishing and cerium treatment complemented earlier results obtained for S31600 and S31603 stainless steels.

- Overall, the extent of crevice corrosion incurred by as-produced N06625 pipe specimens in the present tests was similar to that in some other reported studies.[4,6-8] However, the maximum depth of attack did not replicate that found for some N06625 pipe in at least one test program.[5]

ACKNOWLEDGMENT

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TABLE 1

Chemical Composition of Material Tested*

Ni	Cr	Mo	Fe	Nb+Ta	Al	Ti	Si	C	S	Mn	P
61.33	21.49	8.73	4.52	3.39	0.20	0.20	0.10	0.01	<0.001	0.05	0.005

*   UNS N06625 origin INCO Alloys International, Inc. mill analysis for heat VX1946AK

TABLE 2

Test Matrix

Seawater		Test Duration		Start	Temperature			Specimen Identification				
(NSW)	(CSW)	(60 Days)	(180 Days)	Date	@ Start	Mean	Max.	Controls	E. Pol. (OD)	E. Pol. (OD & ID)	Cerium A	Cerium B
	X	X		4/20/95	19.8°	25.1°	30.0°	001-002 003-004	023, 025 026 ,027	021, 022 024, 030	061, 062 063, 064	081, 082 083, 084
	X	X		6/15/95	25.0°	27.3°	30.0°	005, 006	028, 029	031, 032	065, 066	085, 086
X		X		6/15/95	25.0°	27.3°	30.0°	007, 008	035, 036	033, 034	067, 068	087, 088
X			X	6/15/95	23.0°	26.5°	30.0°	009, 010 011, 012	038, 039 040, 045	037, 041 042, 043	069, 070 071, 072	089, 090 091, 092
X		X		7/20/95 *	29.0°	27.3°	30.0°	013, 014	046, 048	044, 047	073, 074	093, 094
X		X		11/30/95	14.0°	12.1°	17.0°	015, 016	049, 051	050, 052	075, 076	095, 096
X			X	11/30/95	14.0°	14.2°	25.5°	017, 018 019, 020	053, 057 058, 059	054, 055 056, 060	077, 078 079, 080	097, 098 099, 100

* Test performed with 25 mm separation between specimens and main header supply (see discussion).

TABLE 3

Routine Seawater Source Hydrology

Test Period	pH	Salinity (g/L)	Chloride (g/L)	Sulfate (g/L)	Dissolved O₂ (mg/L)
			Range of Results for Indicated Test Periods		
4/20/95 to 10/20/95 (180 days)	7.6-8.1	32.3-37.0	17.9-20.5	2.4-2.8	5.0-7.3
6/15/95 to 8/15/95 (60 days)	7.9-8.0	32.3-37.0	17.9-20.5	2.5-2.8	5.0-6.0
6/15/95 - 12/15/95 (180 days)	7.6-8.0	32.3-37.0	17.9-20.5	2.5-2.8	5.0-8.9
7/20/95 to 9/20/95 (60 days)	7.6-8.0	33.0-37.0	18.3-20.5	2.5-2.8	5.0-6.1
11/30/95 to 1/30/96 (60 days)	8.0-8.1	32.8-35.5	17.0-19.2	2.5-2.7	8.1-9.0
11/30/95 to 5/30/96 (180 days)	8.0-8.1	30.9-35.0	17.1-19.4	2.5-2.7	8.0-10.3

* Other: sulfide <0.005
         ammonia <0.05
         Total Fe 0.04 to 0.20 mg/L

** Overall percent saturation at sample temperature 78.6%-108%

Note: Dissolved O₂ column header reads "Dissolved O_2 (mg/L)".

TABLE 4

Percent of Crevice Sites Attacked Based On Number of Available Specimens in Indicated Tests

Surface Treatment	Percent of Crevices, All Tests (40)	Percent of Vinyl Sleeve Sites (28)	Percent of Rubber Gland Sites (12)	Percent of Sites in Warm NSW (16)	Percent of Sites in Cold NSW (12)	Percent of Sites in CSW (12)
As-Produced	78%	71%	92%	88%	50%	83%
Cerium A	28%	18%	50%	19%	17%	50%
Cerium B	28%	21%	42%	25%	17%	50%
Elec.Pol. - OD	0%	0%	0%	0%	0%	0%
Elec.Pol. - OD/ID	2.5%	0%	8%	0%	0%	8%

TABLE 5

Summary of Earliest Time for In-situ Detection of Crevice Corrosion on Specimens Tested for 60 and 180 Days with Vinyl Sleeves

Natural Sewater Tests				Chlorinated Seawater Tests			
Test Condition	Specimen Identification	Detection Time (days) Site 1	Site 2	Test Condition	Specimen Identification	Detection Time (days) Site 1	Site 2
14.0°C Start[t]	As-produced			19.8°C Start	As-produced		
	016-60	OK	ND*		001-180	5	ND*
	017-180	ND*	OK		002-180	6	5
	018-180	ND*	OK		Cerium A		
					061-180	29	43
					062-180	ND*	25
					Cerium B		
					081-180	ND*	OK
					082-180	ND*	67
25.0°C Start	As-produced			25.0°C Start	As-produced		
	007-60	OK	12		005-60	5	4
	008-60	OK	21		006-60	OK	12
	009-180	ND*	62				
	010-56	ND*	56				
	Cerium A						
	069-180	OK	ND*				
	Cerium B						
	087-60	OK	ND*				
	089-180	OK	ND*				
	090-180	ND*	OK				
29.0°C Start	As-produced						
	013-60	ND*	41				
	014-60	15	27				

* ND = not detected in-situ, but crevice corrosion found at end of test

TABLE 6

Resistance of Various Alloy 625 Pipe Specimens in 60-day Vinyl Sleeve Tests Conducted in Warm Natural (NSW) and Chlorinated (CSW) Seawater at an Initial Temperature of 25.0° C

| Material and Specimen Code | Affected Area (mm^2) | | Maximum Depth of Attack (mm) | |
	Upstream Site	Downstream Site	Upstream Site	Downstream Site
As-Produced				
005-CSW	383	10	<0.01	<0.01
006-CSW	OK	562	<0.01	<0.01
007-NSW	OK	1133	OK	0.20
008-NSW	OK	316	OK	0.18
Cerium A				
065-CSW	OK	OK	OK	OK
066-CSW	OK	OK	OK	OK
067-NSW	OK	OK	OK	OK
068-NSW	OK	OK	OK	OK
Cerium B				
085-CSW	OK	OK	OK	OK
086-CSW	OK	OK	OK	OK
087-NSW	OK	207	OK	<0.01
088-NSW	OK	OK	OK	OK
Elec. Pol.- OD				
028-CSW	OK	OK	OK	OK
029-CSW	OK	OK	OK	OK
035-NSW	OK	OK	OK	OK
036-NSW	OK	OK	OK	OK
Elec. Pol.- ID/OD				
031-CSW	OK	OK	OK	OK
032-CSW	OK	OK	OK	OK
033-NSW	OK	OK	OK	OK
034-NSW	OK	OK	OK	OK

TABLE 7

Resistance of Various Alloy NO6625 Pipe Specimens in 60- and 180-Day Vinyl Sleeve Crevice Tests Conducted in Warm Natural Seawater at an Initial Temperature of 25.0°C

Material and Specimen Code	Affected Area (mm^2)		Maximum Depth of Attack (mm)	
	Upstream Site	Downstream Site	Upstream Site	Downstream Site
As-Produced				
007-60	OK	1133	OK	0.20
008-60	OK	316	OK	0.18
009-180	15	682	<0.01	<0.01
010-180	21	1419	<0.01	<0.01
Cerium A				
067-60	OK	OK	OK	OK
068-60	OK	OK	OK	OK
069-180	OK	13	OK	<0.01
070-180	OK	OK	OK	OK
Cerium B				
087-60	OK	207	OK	<0.01
088-60	OK	OK	OK	OK
089-180	OK	12	OK	<0.01
090-180	32	OK	<0.01	OK
Elec. Pol. - OD				
035-60	OK	OK	OK	OK
036-60	OK	OK	OK	OK
038-180	OK	OK	OK	OK
039-180	OK	OK	OK	OK
Elec. Pol. - ID/OD				
033-60	OK	OK	OK	OK
034-60	OK	OK	OK	OK
037-180	OK	OK	OK	OK
041-180	OK	OK	OK	OK

TABLE 8

Resistance of Various Alloy NO6625 Pipe Specimens
in 60- and 180-Day Vinyl Sleeve Crevice Tests Conducted
in Cold Natural Seawater at an Initial Temperature of 14.0°C

Material and Specimen Code	Affected Area (mm^2)		Maximum Depth of Attack (mm)	
	Upstream Site	Downstream Site	Upstream Site	Downstream Site
As-Produced				
015-60	OK	OK	OK	OK
016-60	OK	105	OK	<0.01
017-180	384	OK	<0.01	OK
018-180	991	OK	<0.01	OK
Cerium A				
075-60	OK	OK	OK	OK
076-60	OK	OK	OK	OK
077-180	OK	OK	OK	OK
078-180	OK	OK	OK	OK
Cerium B				
095-60	OK	OK	OK	OK
096-60	OK	OK	OK	OK
097-180	OK	OK	OK	OK
098-180	OK	OK	OK	OK
Elec. Pol. - OD				
049-60	OK	OK	OK	OK
051-60	OK	OK	OK	OK
053-180	OK	OK	OK	OK
057-180	OK	OK	OK	OK
Elec. Pol. - ID/OD				
050-60	OK	OK	OK	OK
052-60	OK	OK	OK	OK
054-180	OK	OK	OK	OK
055-180	OK	OK	OK	OK

TABLE 9

Resistance of Various Alloy NO6625 Pipe Specimens in 180-Day Compression Fitting Tests Commencing in Warm and Cold Natural Seawater

Material and Specimen Code	Affected Area (mm^2)		Maximum Depth of Attack (mm)	
	Upstream Site	Downstream Site	Upstream Site	Downstream Site
As-Produced				
011-Warm	2835	1319	<0.01	<0.01
012-Warm	2105	2278	0.03	0.04
019-Cold	2486	95	<0.01	<0.01
020-Cold	OK	197	OK	<0.01
Cerium A				
071-Warm	25	OK	<0.01	OK
072-Warm	OK	767	OK	<0.01
079-Cold	OK	114	OK	<0.01
080-Cold	28	OK	<0.01	OK
Cerium B				
091-Warm	OK	OK	OK	OK
092-Warm	OK	185	OK	<0.01
099-Cold	180	OK	<0.01	OK
100-Cold	OK	2055	OK	<0.01
Elec. Pol. - OD				
040-Warm	OK	OK	OK	OK
045-Warm	OK	OK	OK	OK
058-Cold	OK	OK	OK	OK
059-Cold	OK	OK	OK	OK
Elec. Pol. - ID/OD				
042-Warm	OK	OK	OK	OK
043-Warm	OK	OK	OK	OK
056-Cold	OK	OK	OK	OK
060-Cold	OK	OK	OK	OK

TABLE 10

Resistance of Various NO6625 Pipe Specimens
Fitted With Vinyl Sleeves (VS) and Rubber Gland Compression
Fittings (CF) and Exposed to Warm Chlorinated Seawater for 180 Days

Material and Specimen Code	Affected Area (mm^2)		Maximum Depth of Attack (mm)	
	Upstream Site	Downstream Site	Upstream Site	Downstream Site
As-Produced				
001 VS	1310	27	<0.01	<0.01
002 VS	1709	5	<0.01	<0.01
003 CF	55	1364	<0.01	<0.01
004 CF	1820	4	<0.01	<0.01
Cerium A				
061 VS	696	4	<0.01	<0.01
062 VS	7	774	<0.01	<0.01
063 CF	1556	OK	<0.01	OK
064 CF	1348	OK	<0.01	OK
Cerium B				
081 VS	35	OK	<0.01	OK
082 VS	20	709	<0.01	<0.01
083 CF	OK	OK	OK	OK
084 CF	64	57	<0.01	<0.01
Elec. Pol. - OD				
023 VS	OK	OK	OK	OK
025 VS	OK	OK	OK	OK
026 CF	OK	OK	OK	OK
027 CF	OK	OK	OK	OK
Elec. Pol. - ID/OD				
021 VS	OK	OK	OK	OK
022 VS	OK	OK	OK	OK
024 CF	OK	2	OK	<0.01
030 CF	OK	OK	OK	OK

TABLE 11

Resistance of Various Alloy NO6625 Pipe Specimens in 60-Day
Vinyl Sleeve Tests Conducted in Warm Natural Seawater*

Material and Specimen Code	Affected Area (mm^2)		Maximum Depth of Attack (mm)	
	Upstream Site	Downstream Site	Upstream Site	Downstream Site
As-Produced				
007-VSa	OK	1133	OK	0.20
008-VSa	OK	316	OK	0.18
013-VSb	6	843	<0.01	<0.01
014-VSb	132	914	<0.01	0.02
Cerium A				
067-VSa	OK	OK	OK	OK
068-VSa	OK	OK	OK	OK
073-VSb	OK	OK	OK	OK
074-VSb	OK	OK	OK	OK
Cerium B				
087-VSa	OK	207	OK	<0.01
088-VSa	OK	OK	OK	OK
093-VSb	OK	OK	OK	OK
094-VSb	OK	OK	OK	OK
Elec. Pol. - OD				
035-VSa	OK	OK	OK	OK
036-VSa	OK	OK	OK	OK
046-VSb	OK	OK	OK	OK
048-VSb	OK	OK	OK	OK
Elec. Pol. - ID/OD				
033-VSa	OK	OK	OK	OK
034-VSa	OK	OK	OK	OK
044-VSb	OK	OK	OK	OK
047-VSb	OK	OK	OK	OK

*   Initial seawater temperatures for Vsa and Vsb tests was 25.0° C and 29.0° C, respectively.

TABLE 12

Corrosion Potentials for Duplicate Specimens
at Conclusion of 60-Day Vinyl Sleeve Tests

Environments and Materials	mV vs Ag/AgCl/Seawater Reference Electrode[1]
Warm CSW Start	
As-produced	12, -40
Electropolished OD	362, 360
Electropolished OD/ID	387, 385
Cerium A	375, 373
Cerium B	376, 375
Warm NSW Start[2]	
As-produced	186, 158
Electropolished OD	383, 384
Electropolished OD/ID	391, 393
Cerium A	382, 379
Cerium B	381, 383
Cold NSW Start	
As-produced	315, 194
Electropolished OD	291, 311
Electropolished OD/ID	328, 337
Cerium A	335, 310
Cerium B	316, 315

1 Underlined data correspond to crevice corroded specimens
2 Data shown obtained @ 1000 hours

TABLE 13

Corrosion Potentials for Duplicate Pipe Specimens
at Conclusion of Indicated 180-Day Tests

Environments and Materials	mV vs Ag/AgCl/Seawater Reference Electrode[1]	
	Vinyl Sleeve Crevices	Compression Fittings
Cool CSW Start		
As-produced	8, 25	326, 122
Electropolished OD	369, 368	362, 366
Electropolished OD/ID	390, 390	381, 380
Cerium A	-8, -18	362. -80
Cerium B	371, 84	360, 362
Warm NSW Start		
As-produced	-6, 19	189. 275
Electropolished OD	356, 357	358, 367
Electropolished OD/ID	376, 382	368, 376
Cerium A	356, 359	352. -54
Cerium B	357, 358	356, 324
Cold NSW Start		
As-produced	113, 208	356, -42
Electropolished OD	386, 387	386, 358
Electropolished OD/ID	394, 404	390, 395
Cerium A	387, 384	274, 375
Cerium B	383, 383	110, 287

1   Underlined data correspond to crevice corroded specimens

TABLE 14

SEM/EDS Analyses of Test Material at Indicated Locations[1]

| | N06625 Mill Heat Analysis | As-Produced Pipe | | Electropolished Pipe | |
		Center (Bulk)	Surface	Center (Bulk)	Surface
Ni	61.3	65.1	78.2	64.9	65.7
Cr	21.5	20.5	10.2	20.7	20.8
Mo	8.7	10.2	7.9	10.2	9.7
Fe	4.5	3.2	3.4	3.3	3.0
Other[2]	4.0				
	100.0	99.0	99.7	99.1	99.2

1) Same instrumentation used in reference 9
2) Refer to Table 1 for Nb, Al, Ti, Si and Mn levels

TABLE 15

SEM/EDS Analyses of Test Material at Indicated Locations[1]

| | N06625 Mill Heat Analysis | As-Produced Pipe | | Surface Analysis of Pipes | | |
		Center (bulk)	Surface	Electro-polished	Cerium A	Cerium B
Ni	61.3	64.6	76.7	64.7	75.2	76.0
Cr	21.5	23.4	12.0	23.3	12.9	12.6
Mo	8.7	6.8	6.2	7.2	6.8	6.1
Fe	4.5	5.1	5.2	4.9	5.1	5.4
Other	4.0					
Total	100.0	99.9	100.1	100.1	100.0	100.1

[1] = In-house EDS results

TABLE 16

Normalized EDS Results

	N06625 Pipe Heat Analysis	As-Produced Pipe		Surface Analyses		
		Center	Surface	Electro-Polished	Cerium A	Cerium B
Table 15 ref						
Cr	21.5	21.5	10.1	21.4	11.0	10.7
Mo	8.7	8.7	8.1	9.2	8.7	8.0
(%Cr+3.3x%Mo)	50.2	50.2	36.8	51.9	39.7	37.1
Table 14 ref						
Cr	21.5	21.8	11.7	22.3		
Mo	8.7	8.7	6.4	8.2		
(%Cr+3.3x%Mo)	50.2	50.5	32.8	49.4		
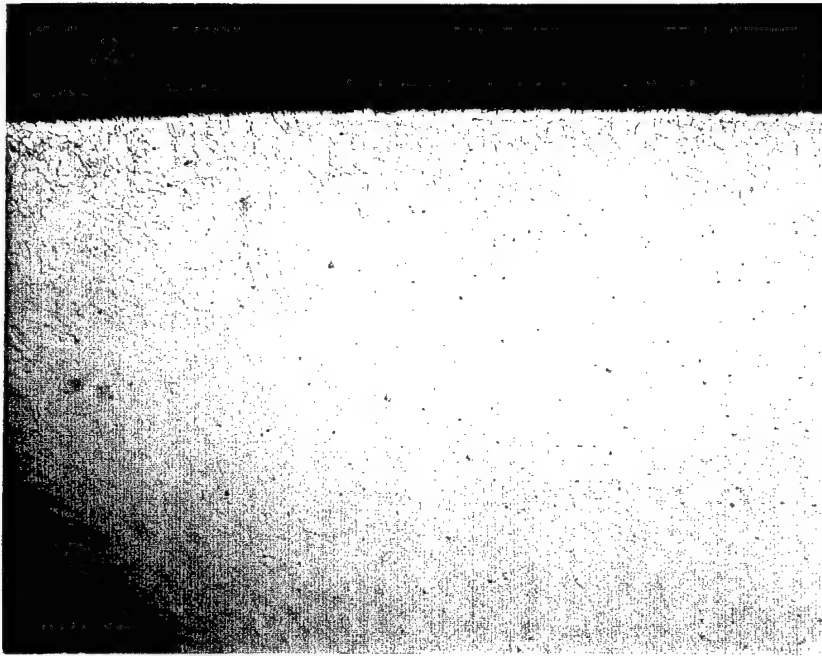
(a) 100X (differential interferrence contrast)   97459-1
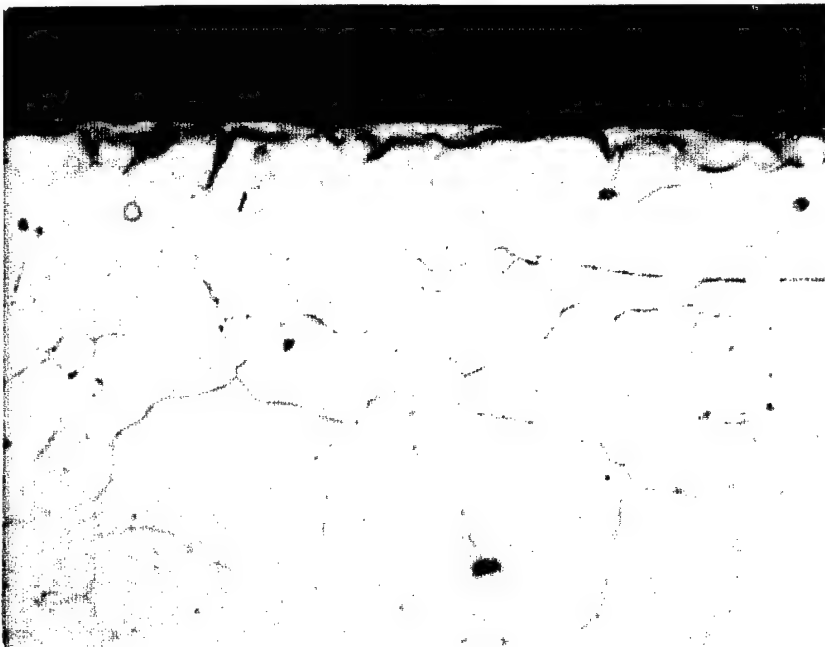
(b) 1000X   97459-3

Figure 1.   Etched microstructure of N06625 pipe tested
             (electrolytic chromic-acetic acid etchant)
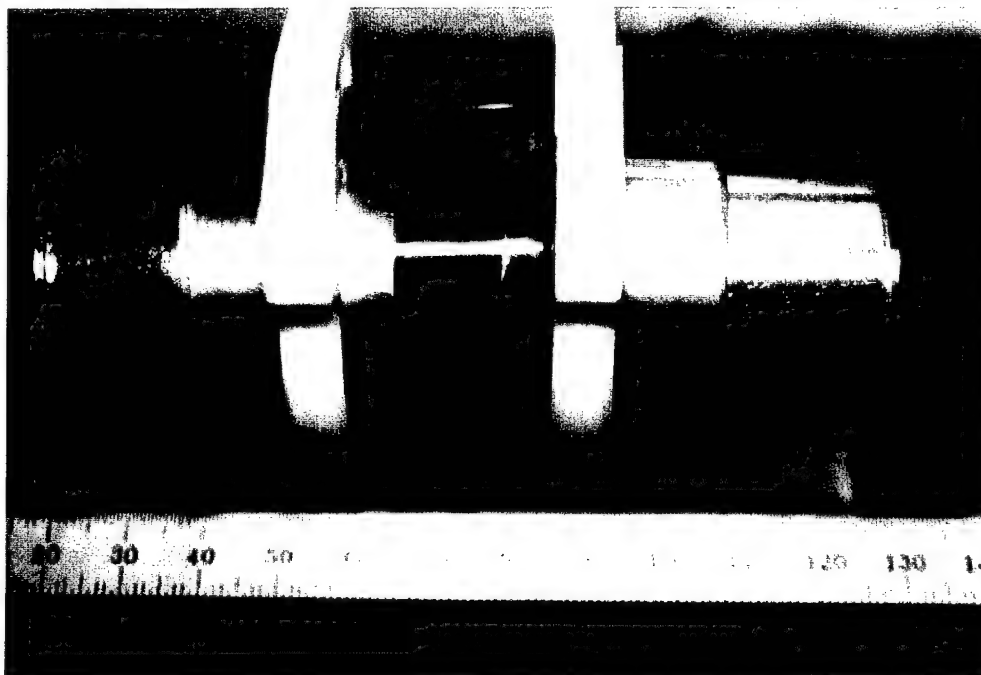
(a)   95199-0A
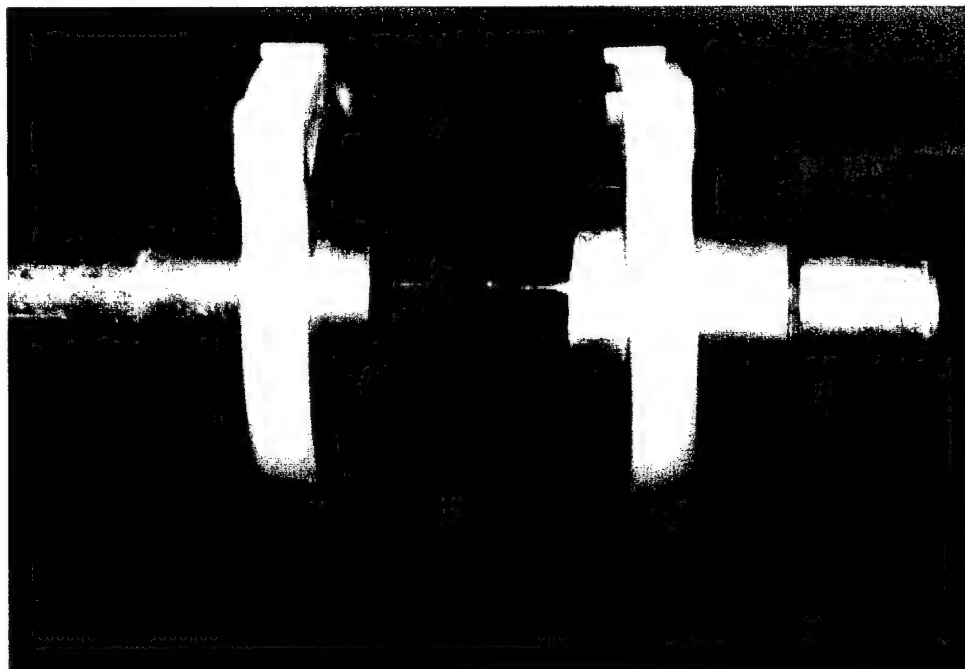
(b)   95199-19A

Figure 2.   Typical appearance of N06625 pipe specimens exposed with
             nominal 13 mm (a) and 25.4 mm (b) spacing in vinyl sleeve
             assemblies.
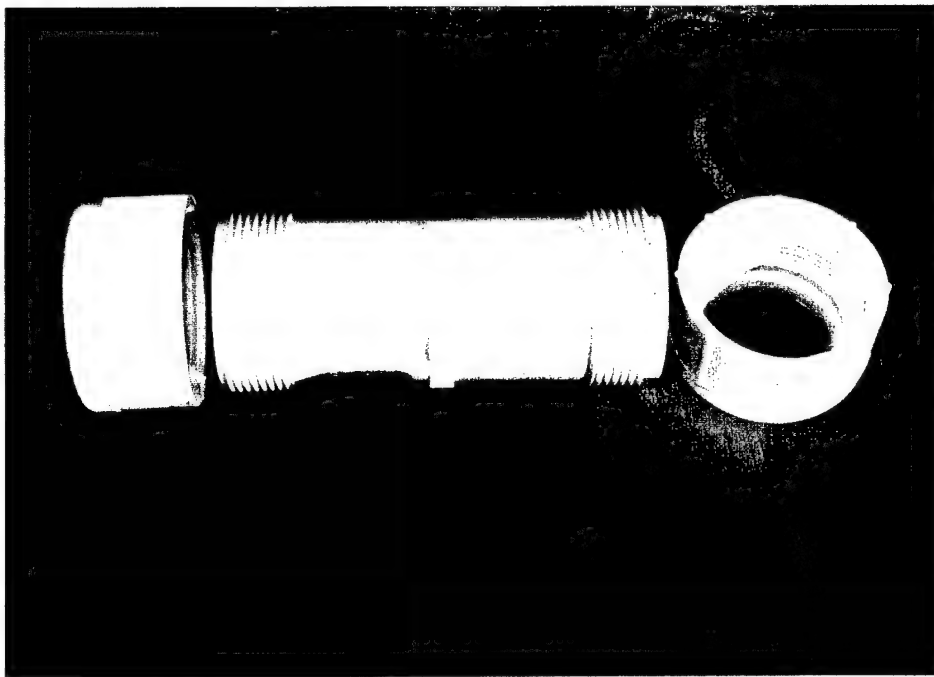
97484-8

Figure 3.   "Exploded" view of a compression fitting assembly.
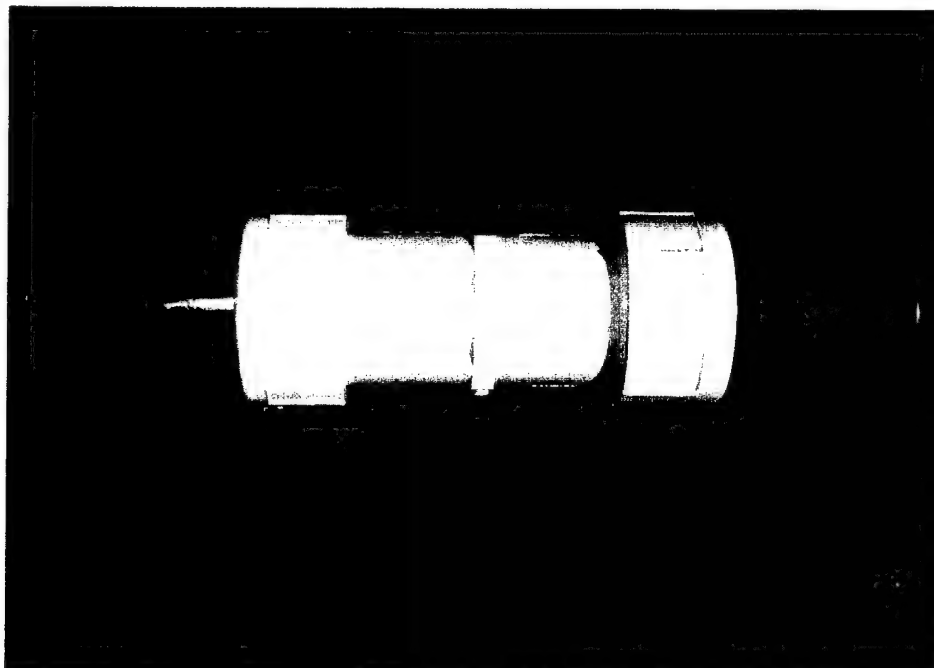
97465-23A

Figure 4.   Typical view of a completed compression fitting assembly.
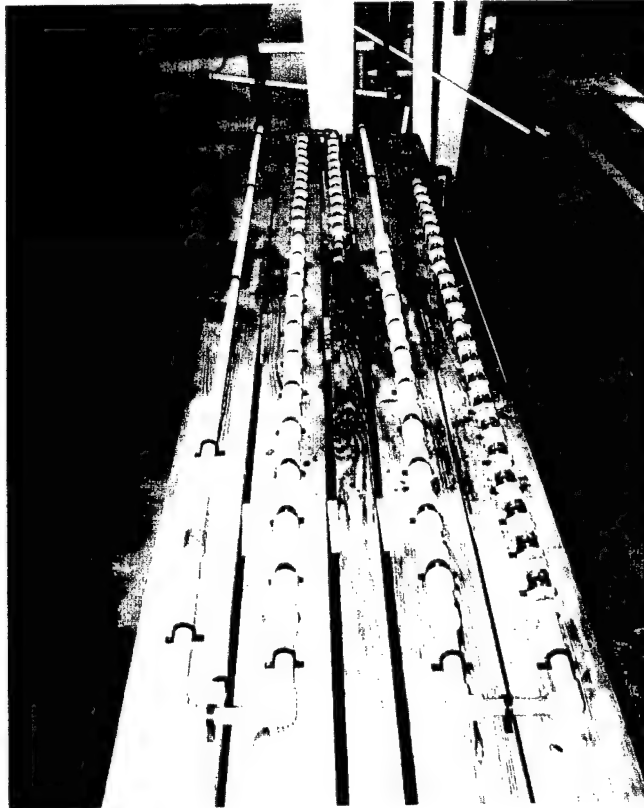
95150-21A

Figure 5.   Overall view of completed test assembly comprising pipe
specimens with vinyl sleeves (right and rear) and PVC
compression fittings with rubber glands (center foreground).
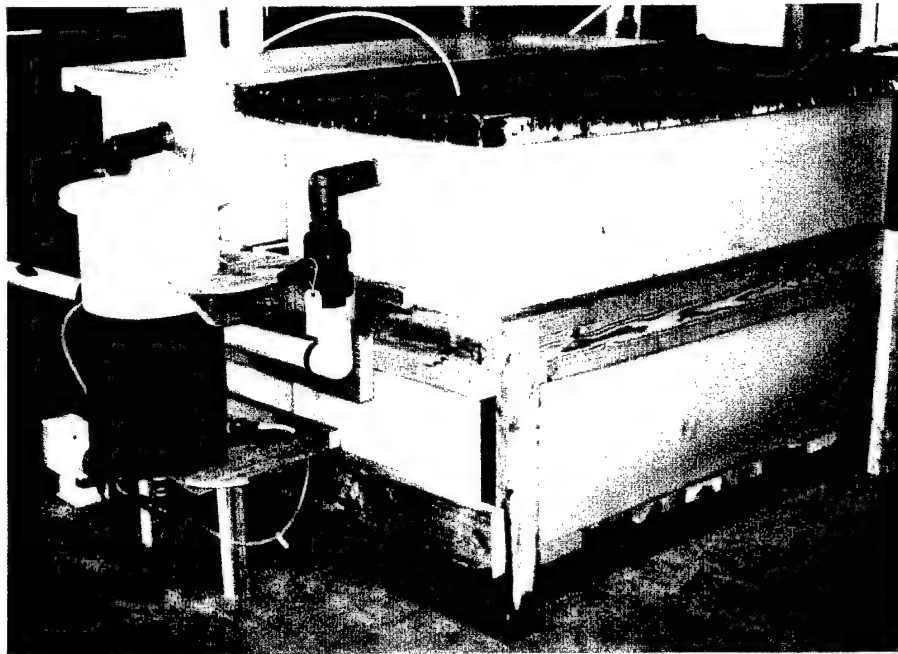
95150-3A
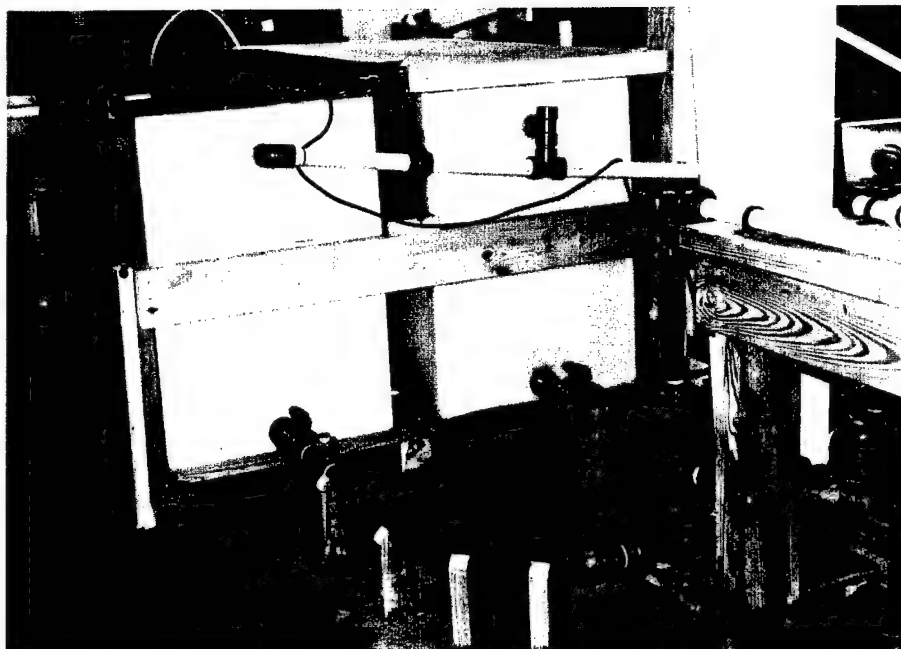
95150-12A

Figure 6.   Head tanks used to supply once-through natural and chlorinated
seawater to crevice corrosion test assemblies. Hypochlorite
reservoir and metering pump shown in top photograph.
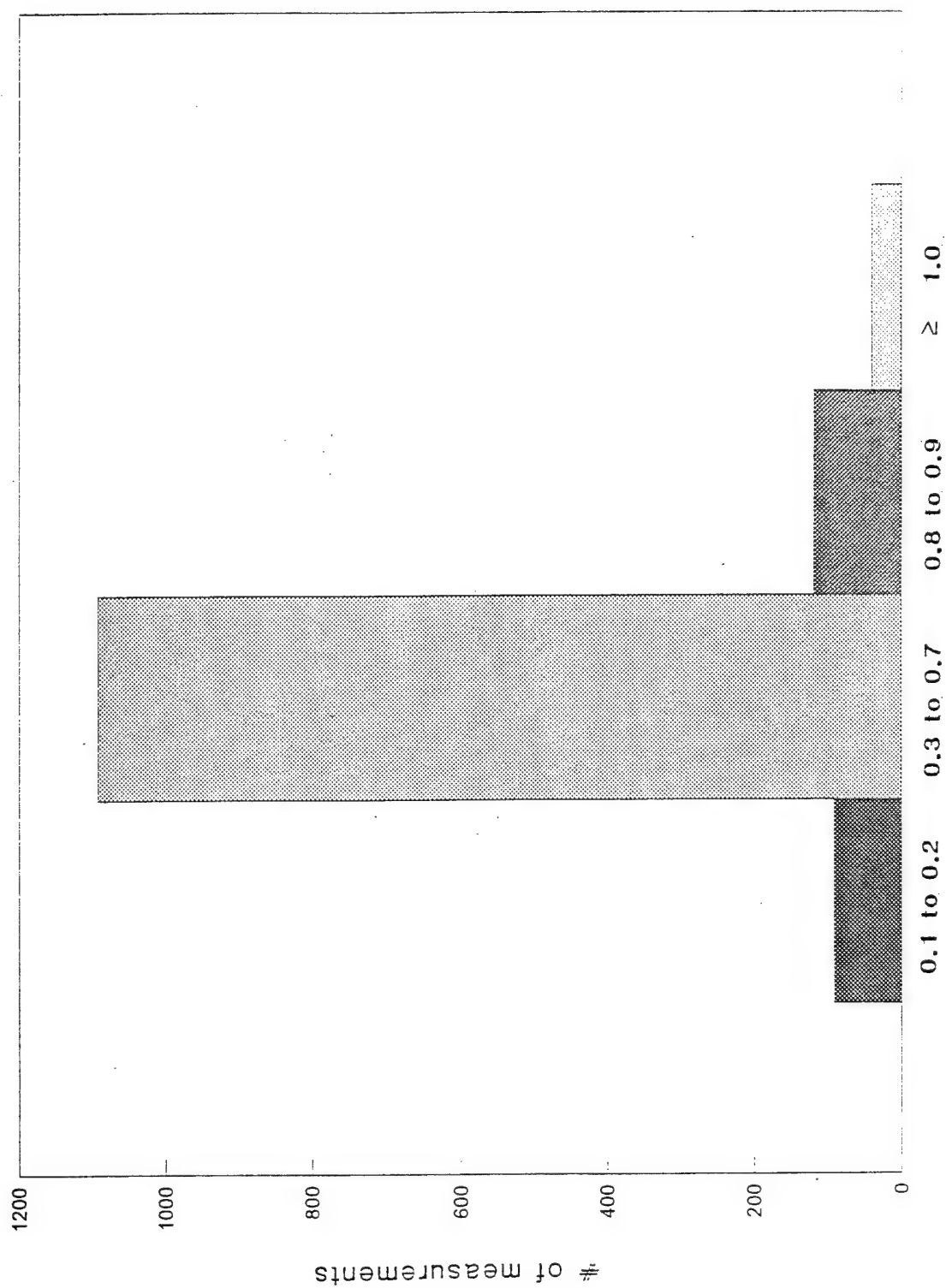
Figure 7. Distribution plot of FAC analyses during 180 day chlorinated seawater test.
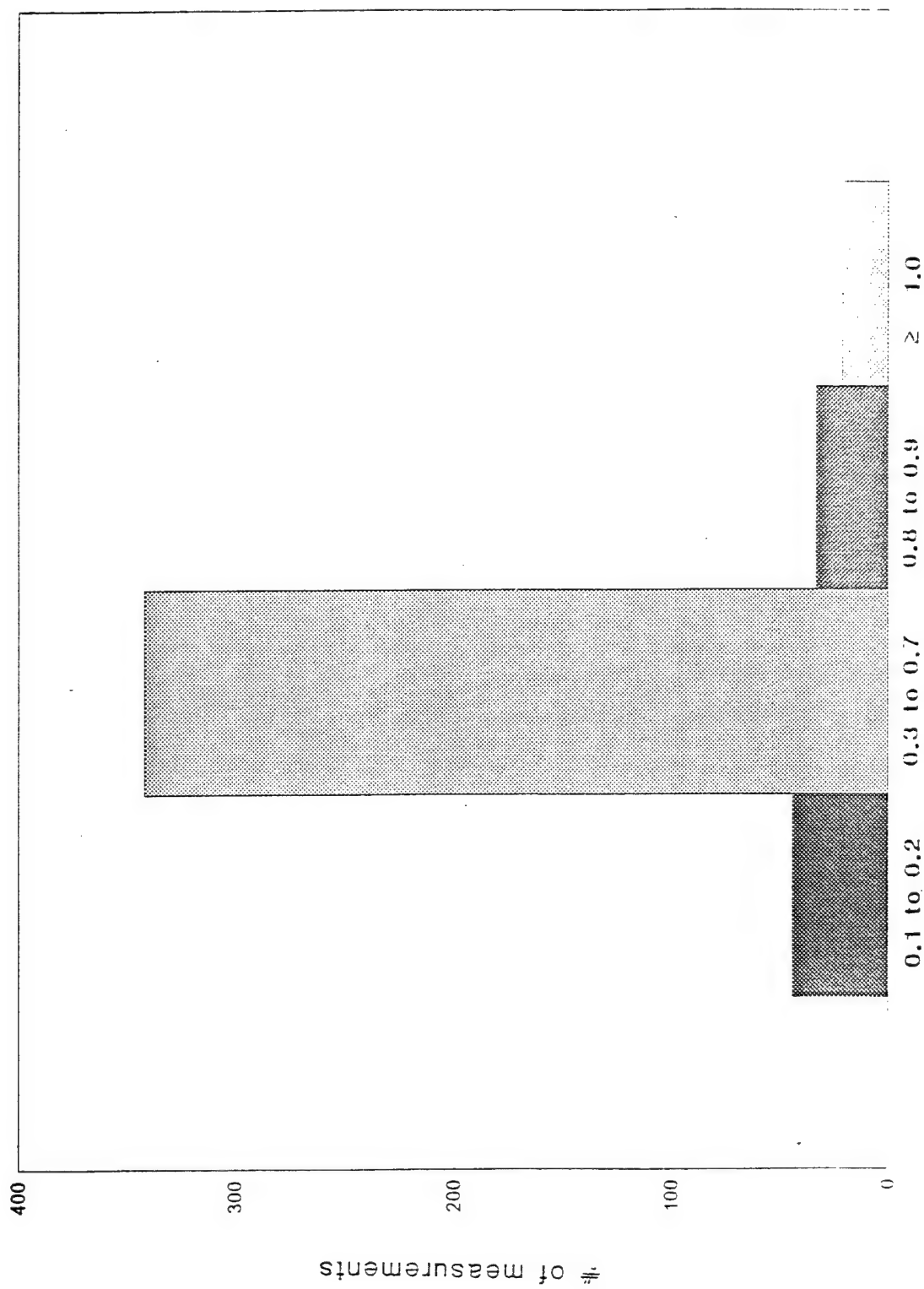
Figure 8. Distribution plot of FAC analyses during 60 day chlorinated seawater test.
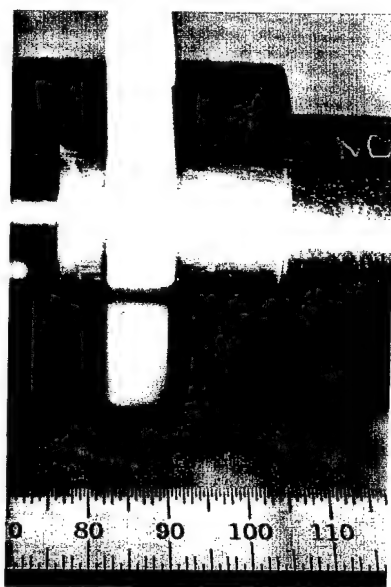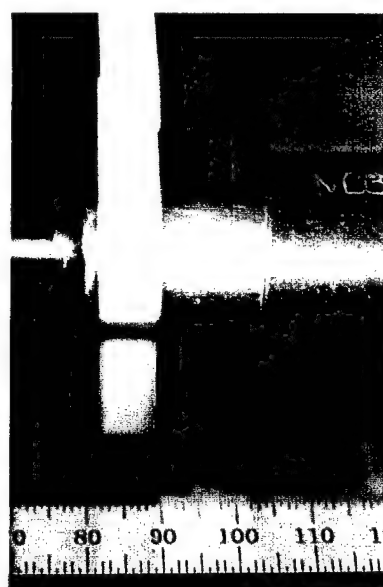
7 days   95103-1   14 days   95115-5
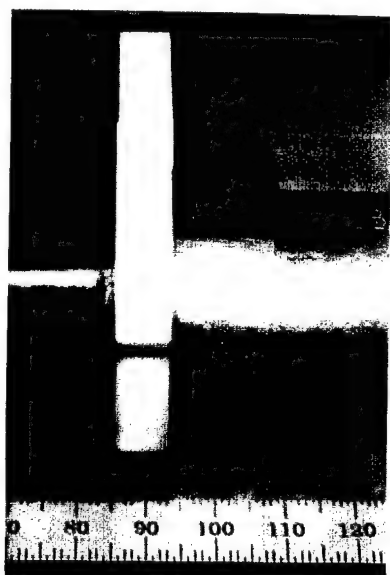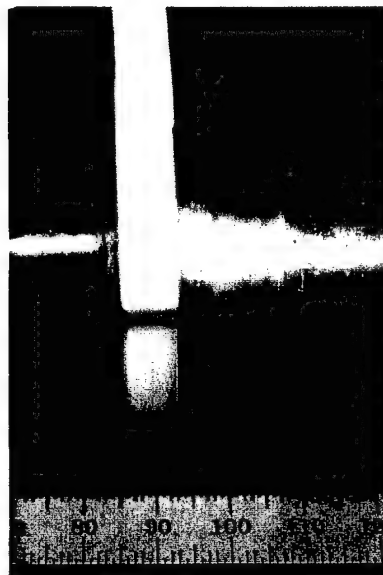
42 days   95126-13A   180 days   95269-12

Figure 9.   Progression of crevice corrosion for as-produced pipe specimen (No. 002) during 180-day exposure to chlorinated seawater with vinyl sleeve crevice formers.
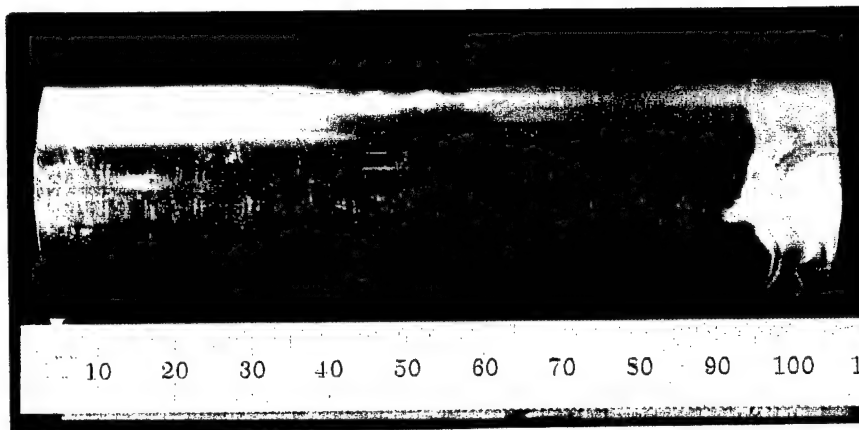
95220-18
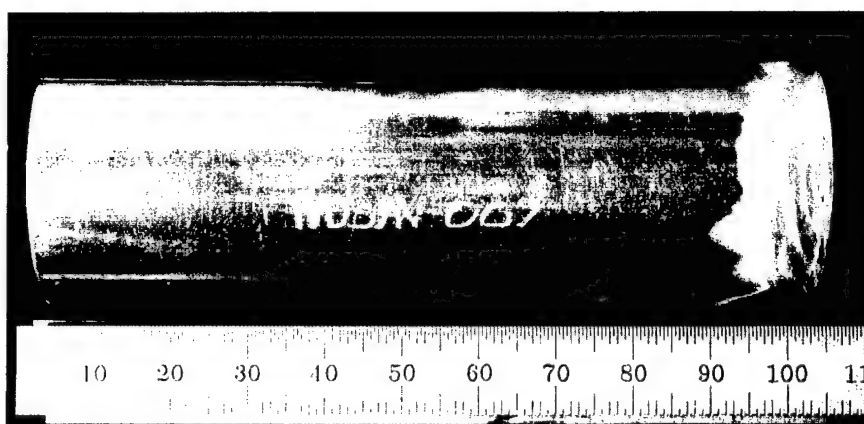
95220-1

Figure 10. After cleaning views showing examples of crevice corrosion incurred by as-produced pipe specimens in 60-day tests with vinyl sleeve crevice formers:
a)   No. 006 - warm chlorinated seawater
b)   No. 007 - warm natural seawater
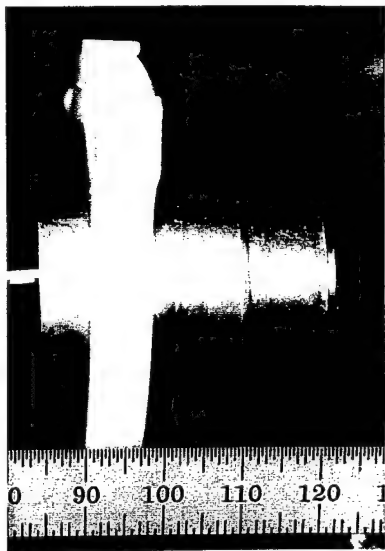
96135-3
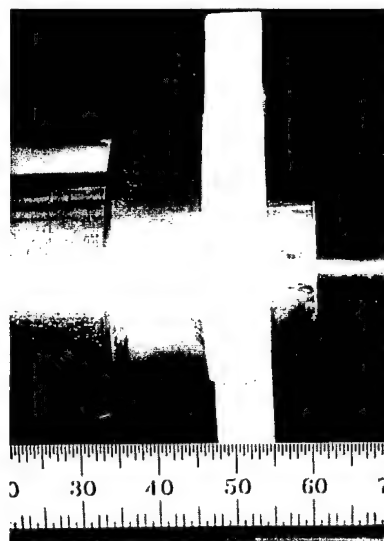
96135-9

Figure 11. In-situ views showing crevice corrosion incurred by two as-produced pipe specimens, l) No. 017 and r) No. 018, during a 180-day exposure to cold, natural seawater with vinyl sleeve crevice formers.
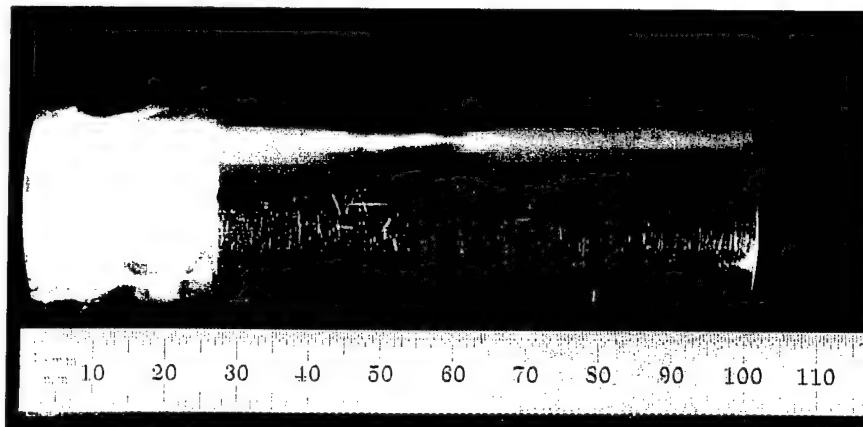
96145-12A
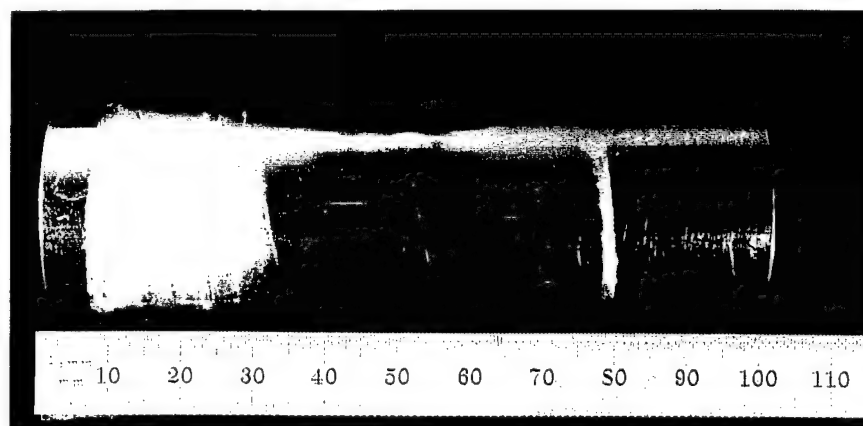
96145-15A

Figure 12.   After cleaning views of as-produced pipe specimens showing extent of crevice corrosion incurred during 180-day cold natural seawater test:
a)   No. 018 - vinyl sleeve
b)   No. 019 - rubber gland compression fitting
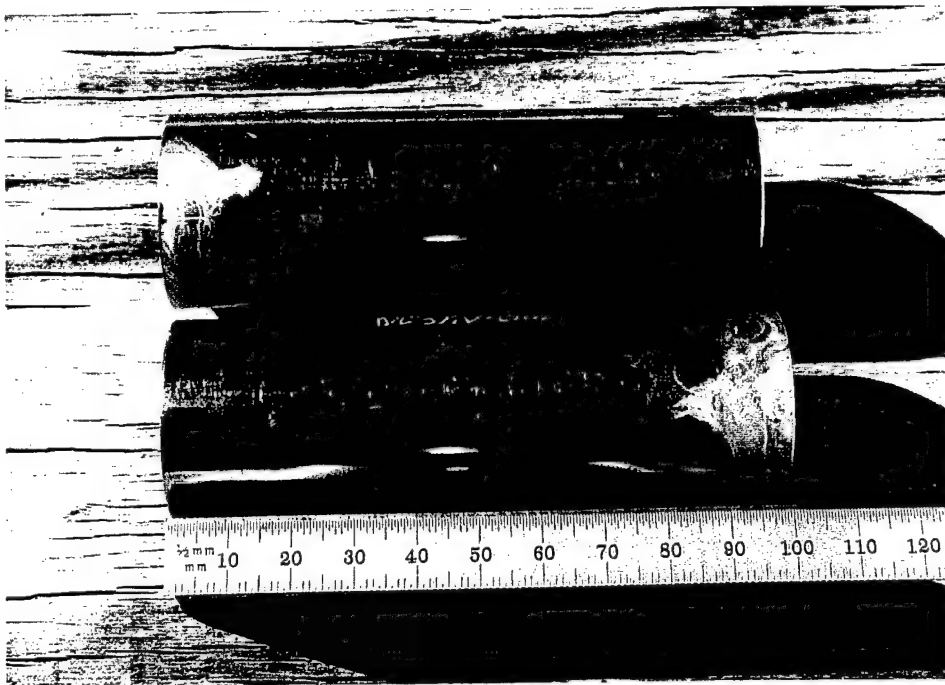
95285-1

Figure 13.   After-cleaning view of as-produced pipe specimens, No. 001 and No. 002, following 180-day exposure to chlorinated seawater with vinyl sleeve crevice formers.
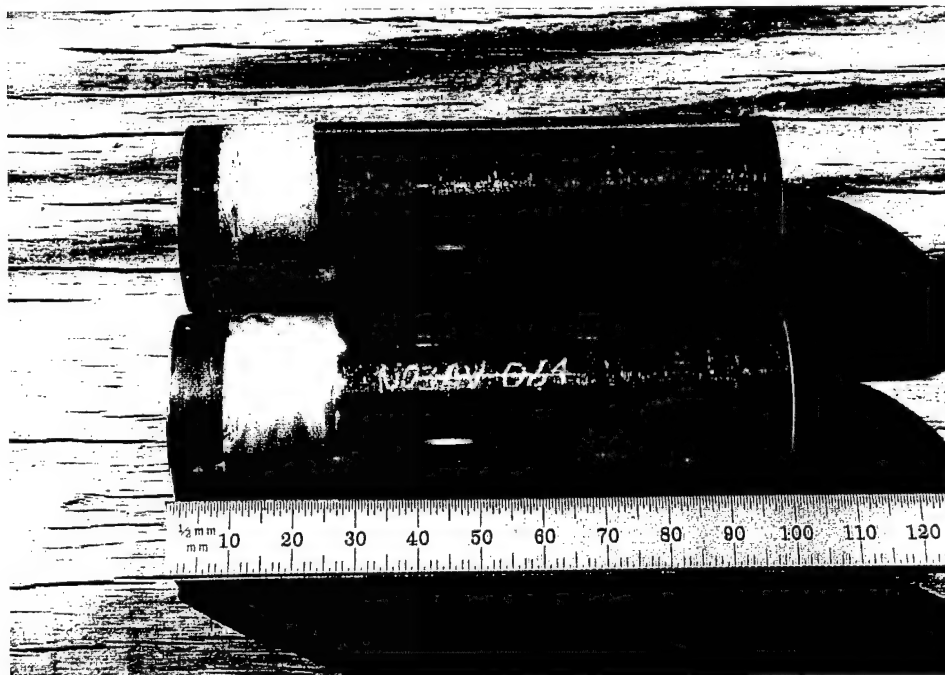
95285-23

Figure 14.   After-cleaning view of Cerium (A) treated pipe specimens, No. 063 and No. 064, following 180-day exposure to chlorinated seawater with rubber gland type compression fittings.
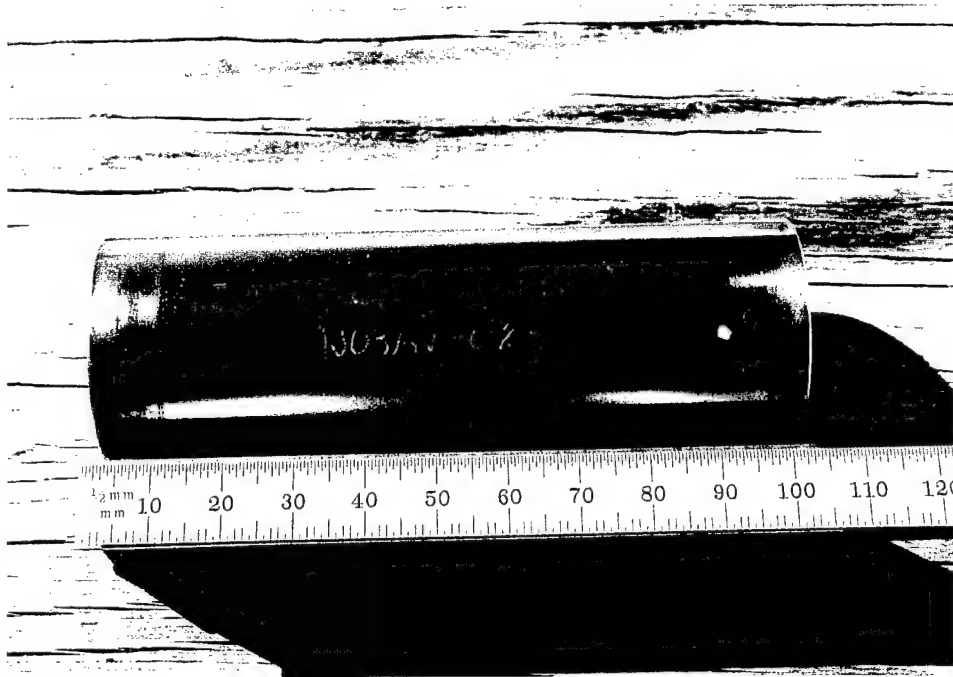
95286-7A

Figure 15. Post test view of electropolished pipe specimen No. 024, after 180-day exposure to chlorinated seawater with rubber gland type compression fitting.
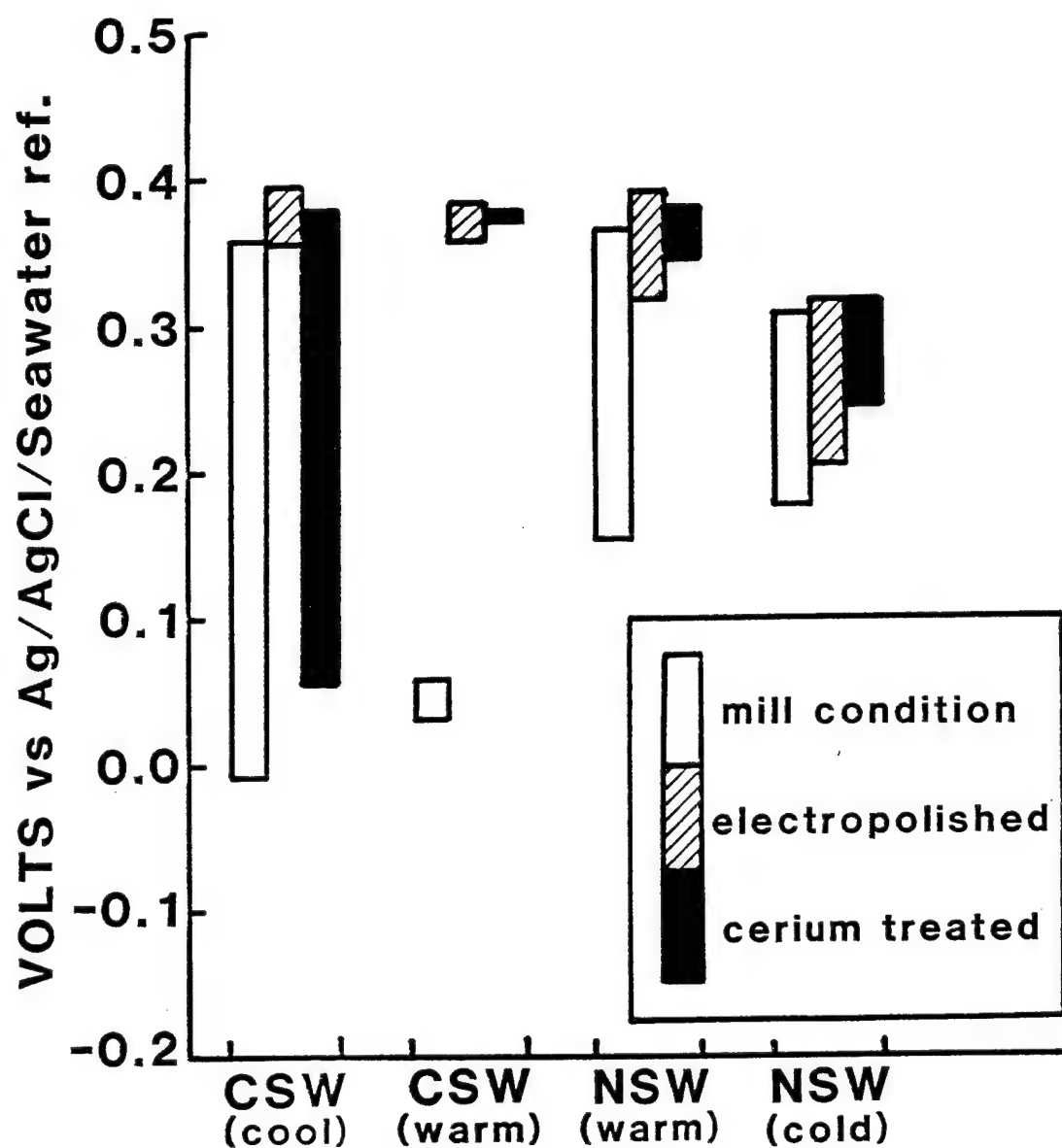
Figure 16.   Range of corrosion potentials for various specimen groups after 1000 hours exposure in chlorinated (CSW) and natural (NSW) seawater tests commencing at different times of the year (left - Spring, center - Summer, and right - Winter).
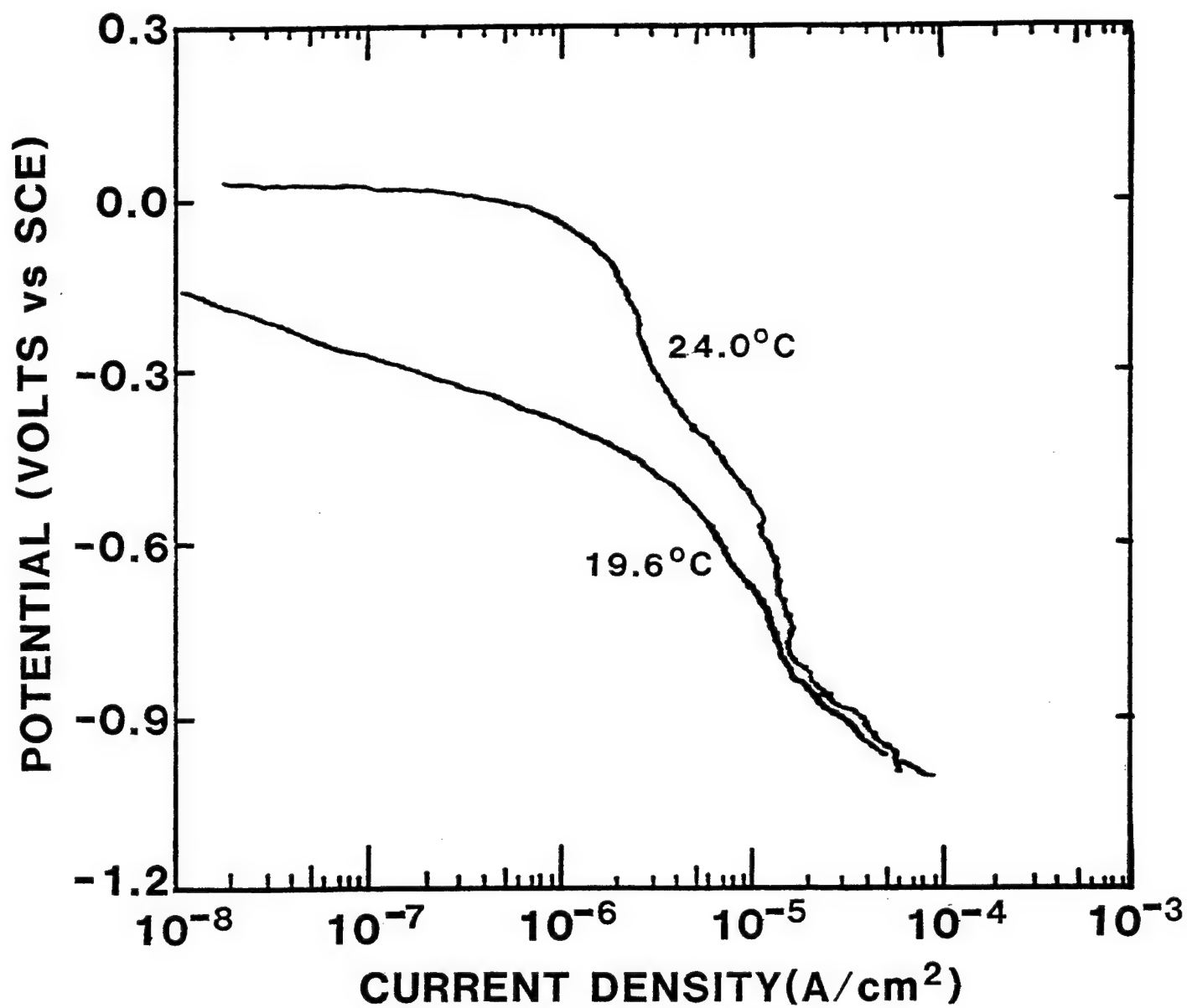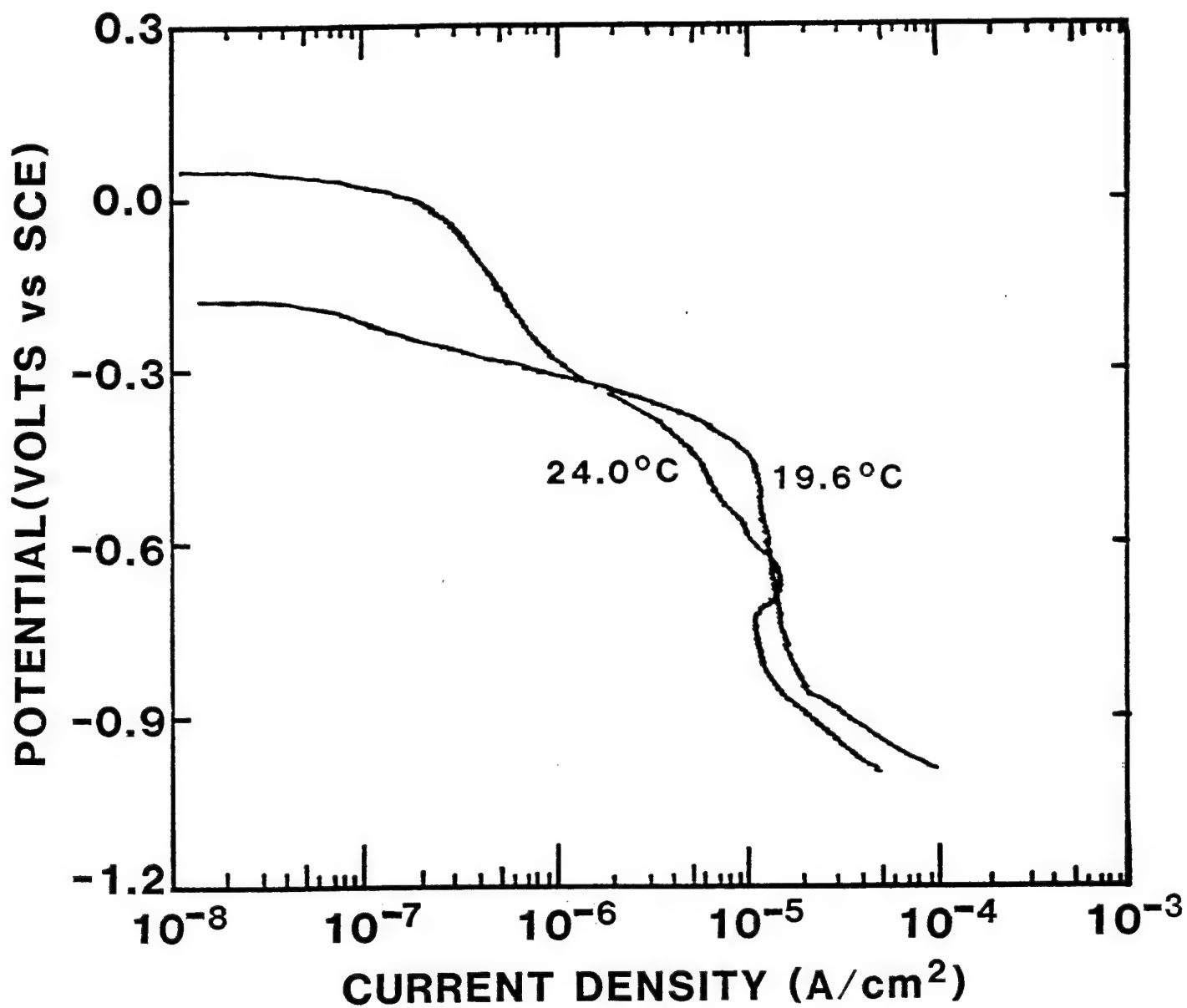
Figure 17.   Cathodic polarization behavior for as-produced N06625 pipe pre-
exposed to ambient temperature seawater for 12 days.
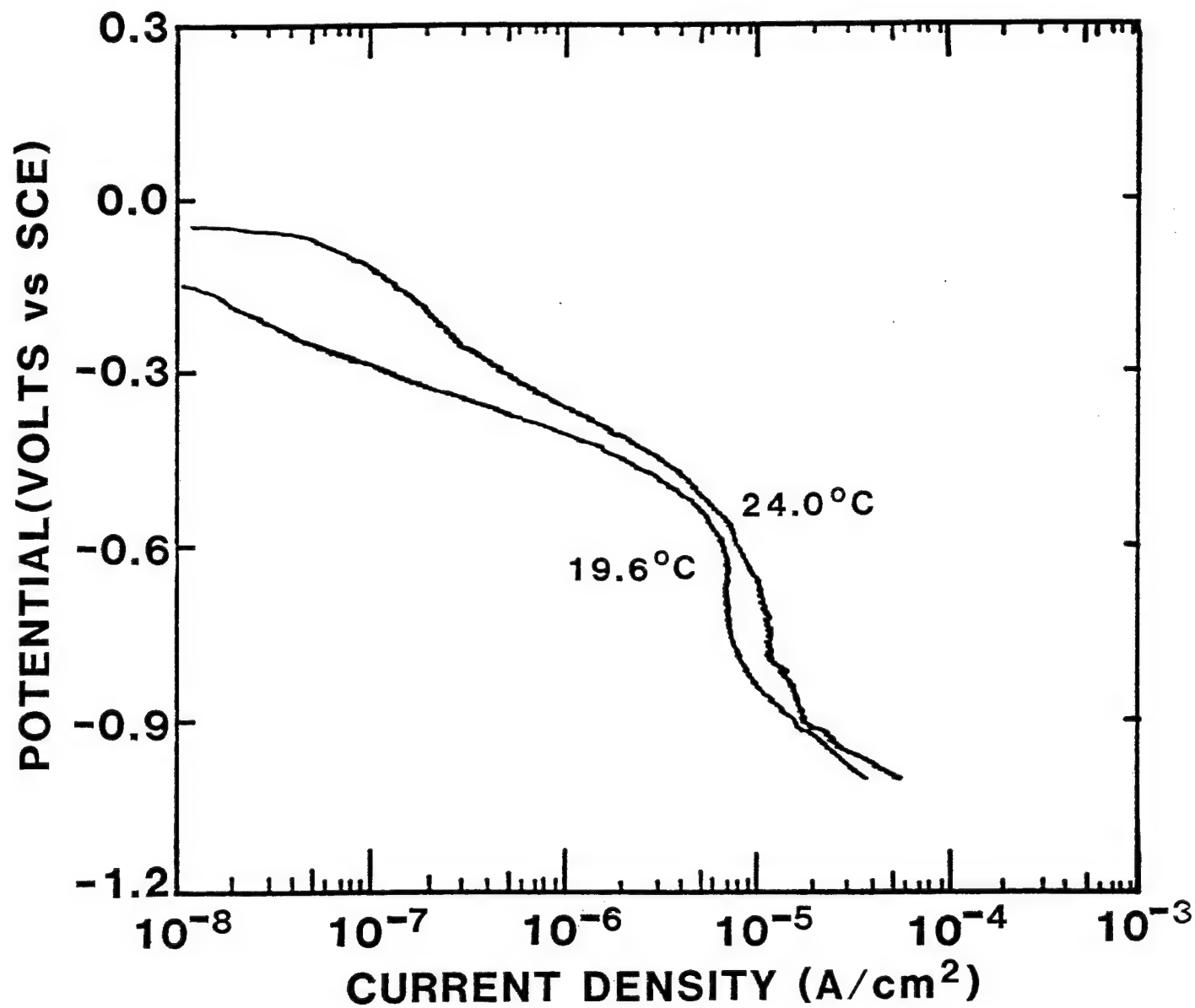
Figure 18.   Cathodic polarization behavior for electropolished N06625 pipe pre-exposed to ambient temperature seawater for 12 days.

Figure 19. Cathodic polarization behavior of cerium (A) treated N06625 pipe pre-exposed to ambient temperature seawater for 12 days.
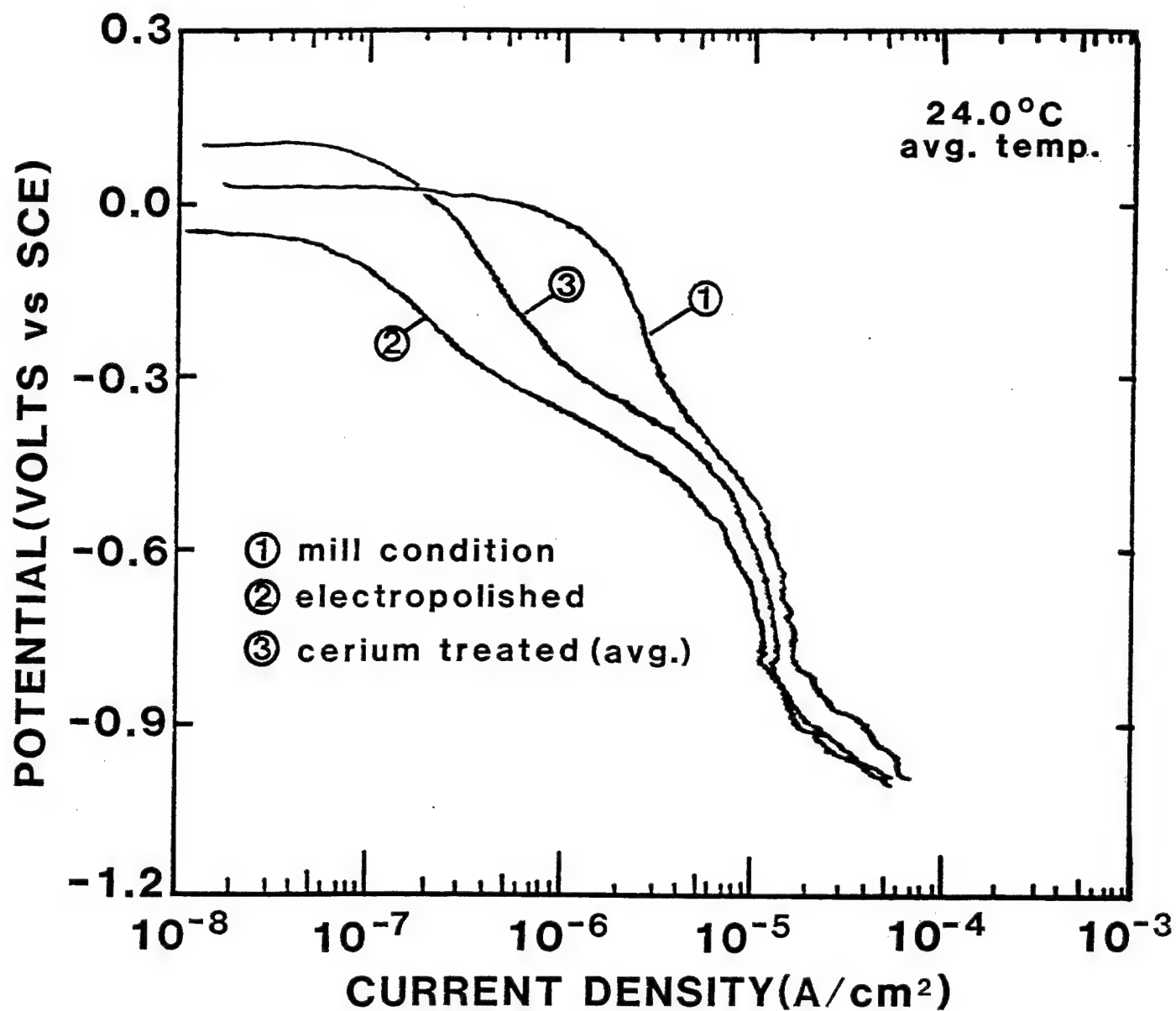
Figure 20.   Cathodic polarization curves for as-produced, electropolished and
cerium treated N06625 pipe pre-exposed to ambient temperature
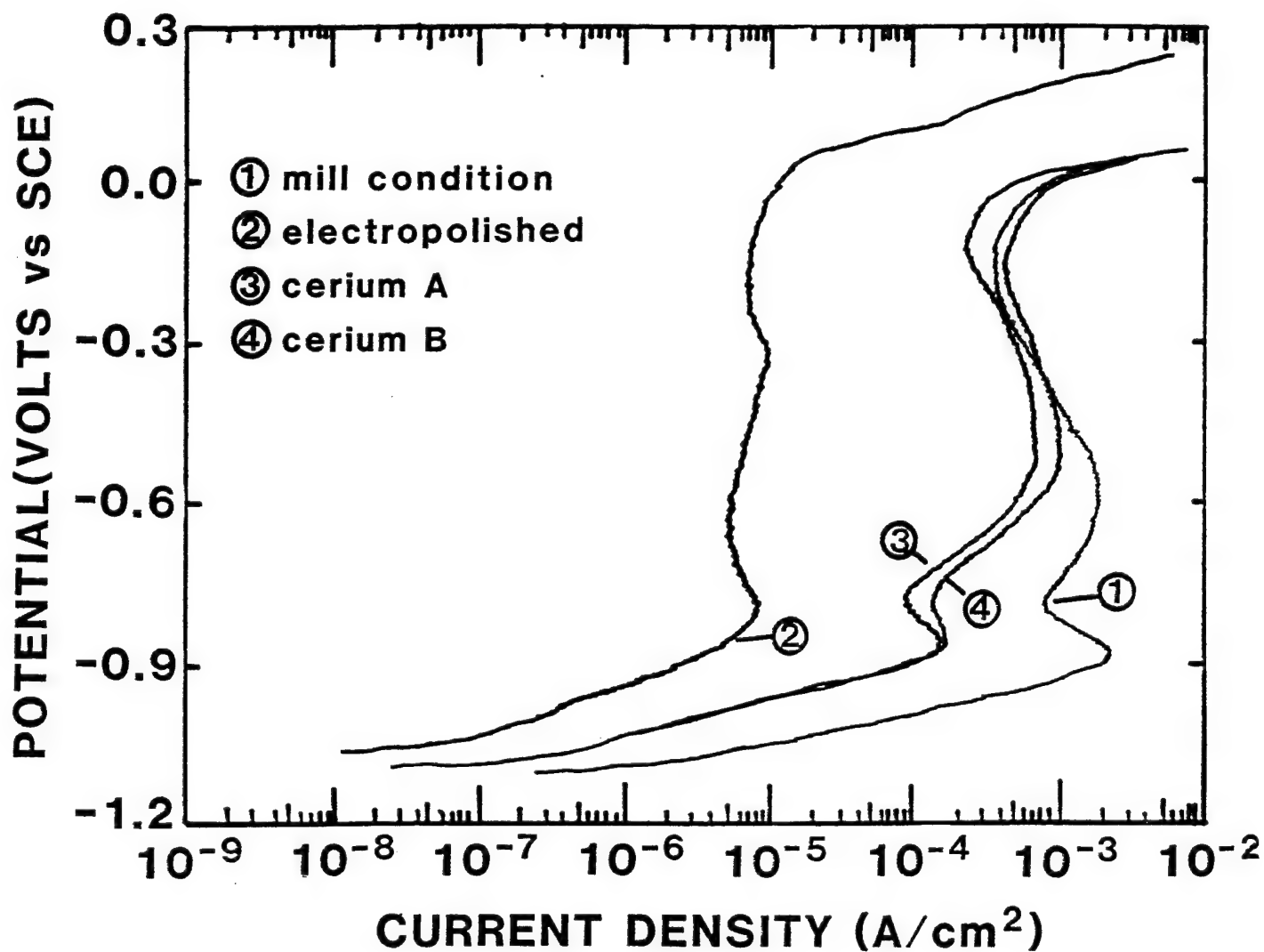seawater for 12 days.

Figure 21. Anodic polarization curves for as-produced, electropolished and cerium treated N06625 pipe in a deaerated, simulated crevice solution at pH = 0.2 (17 mV/min., scan rate).
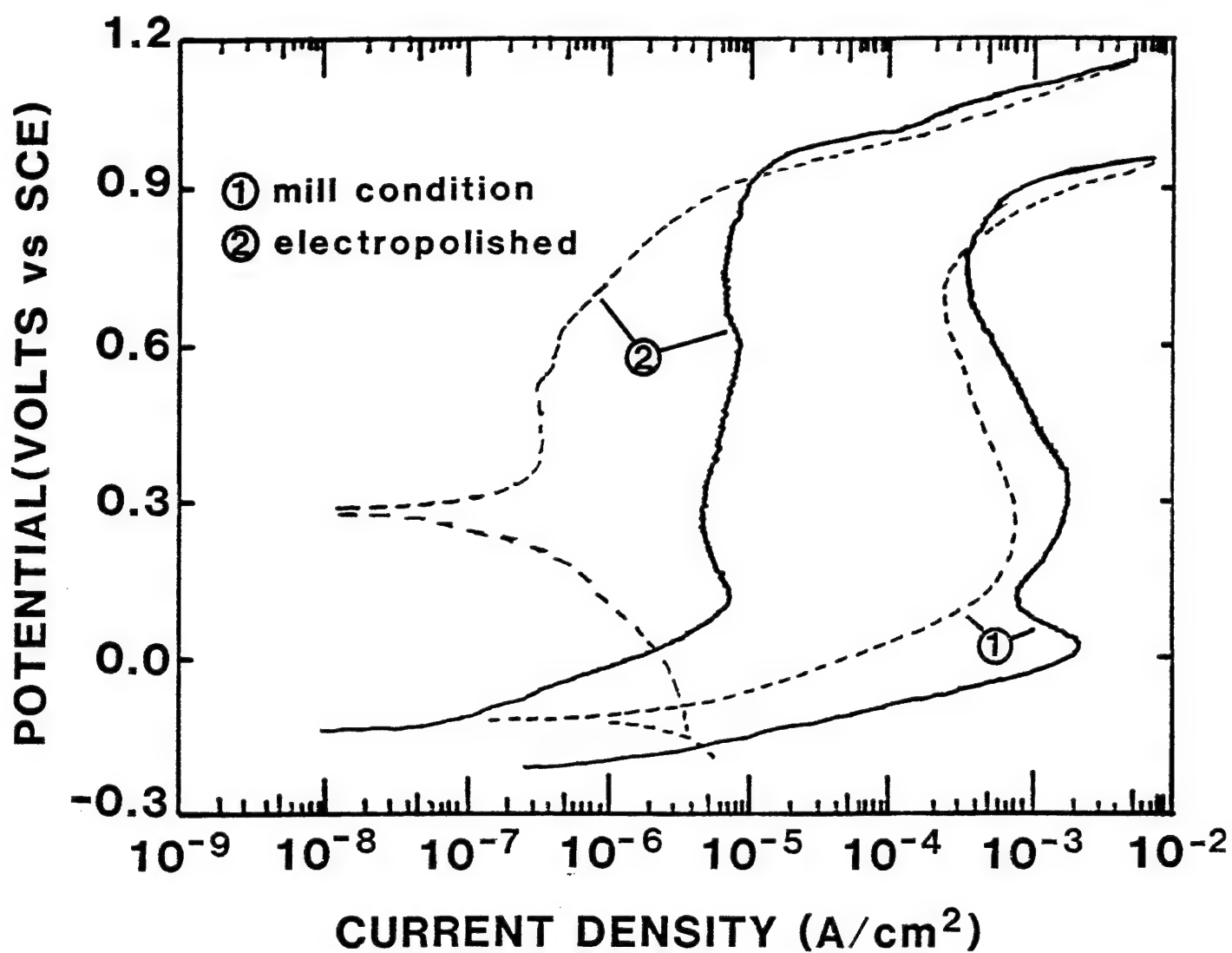
Figure 22. Cyclic forward (solid) and reverse (dashed) scan polarization curves for as-produced and electropolished N06625 pipe in deaerated, simulated crevice solution at pH = 0.2 (scan rate = 17 mV/min.).
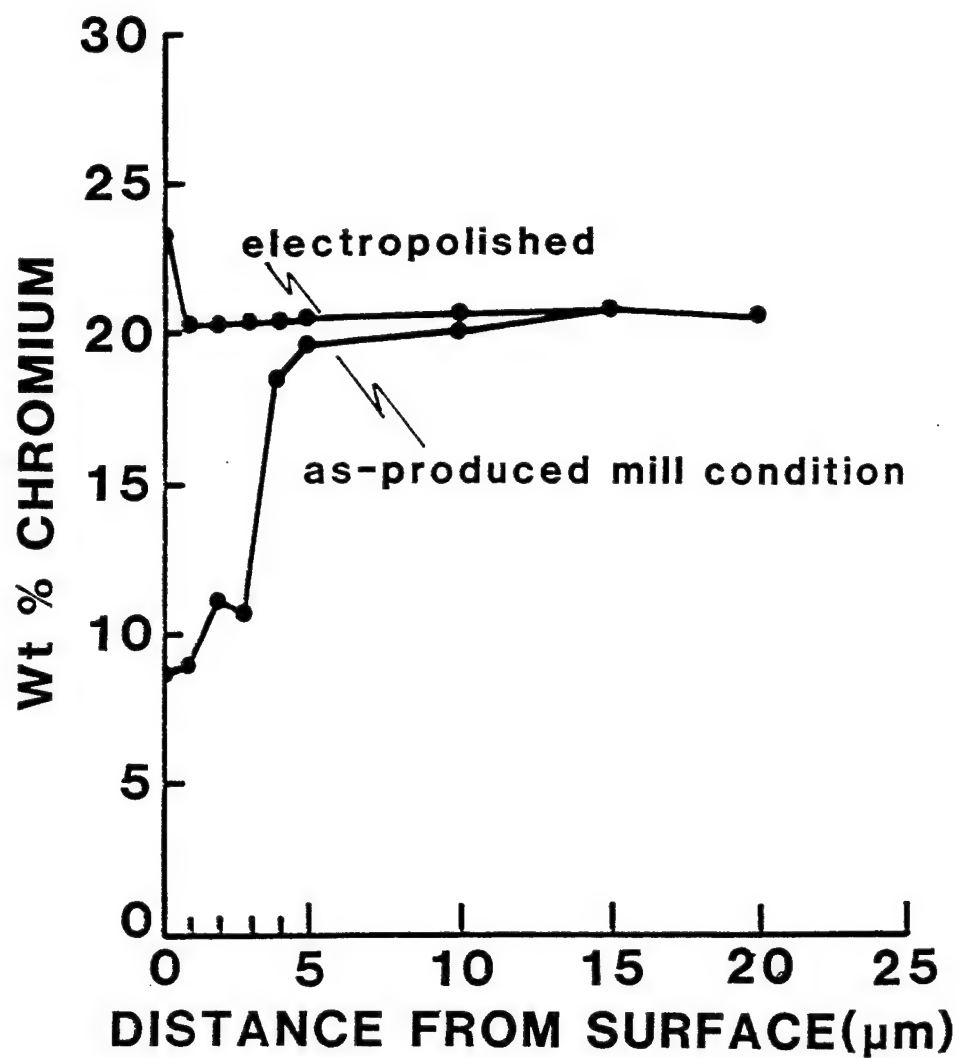
Figure 23. SEM/EDS profiling analyses of cross-sectioned N06625 pipe with and without electropolishing.
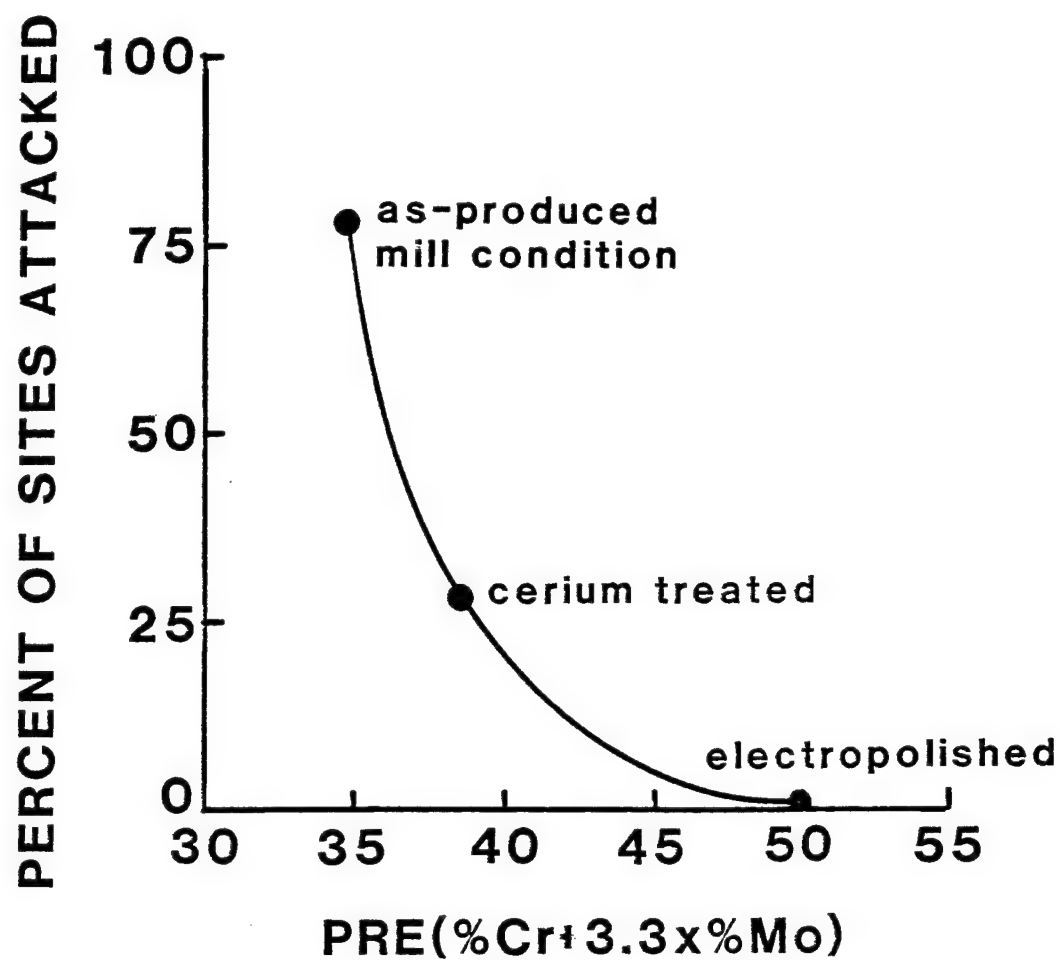
Figure 24.   Relationship between surface PRE value and total number of N06625 crevice sites attacked in various seawater tests.
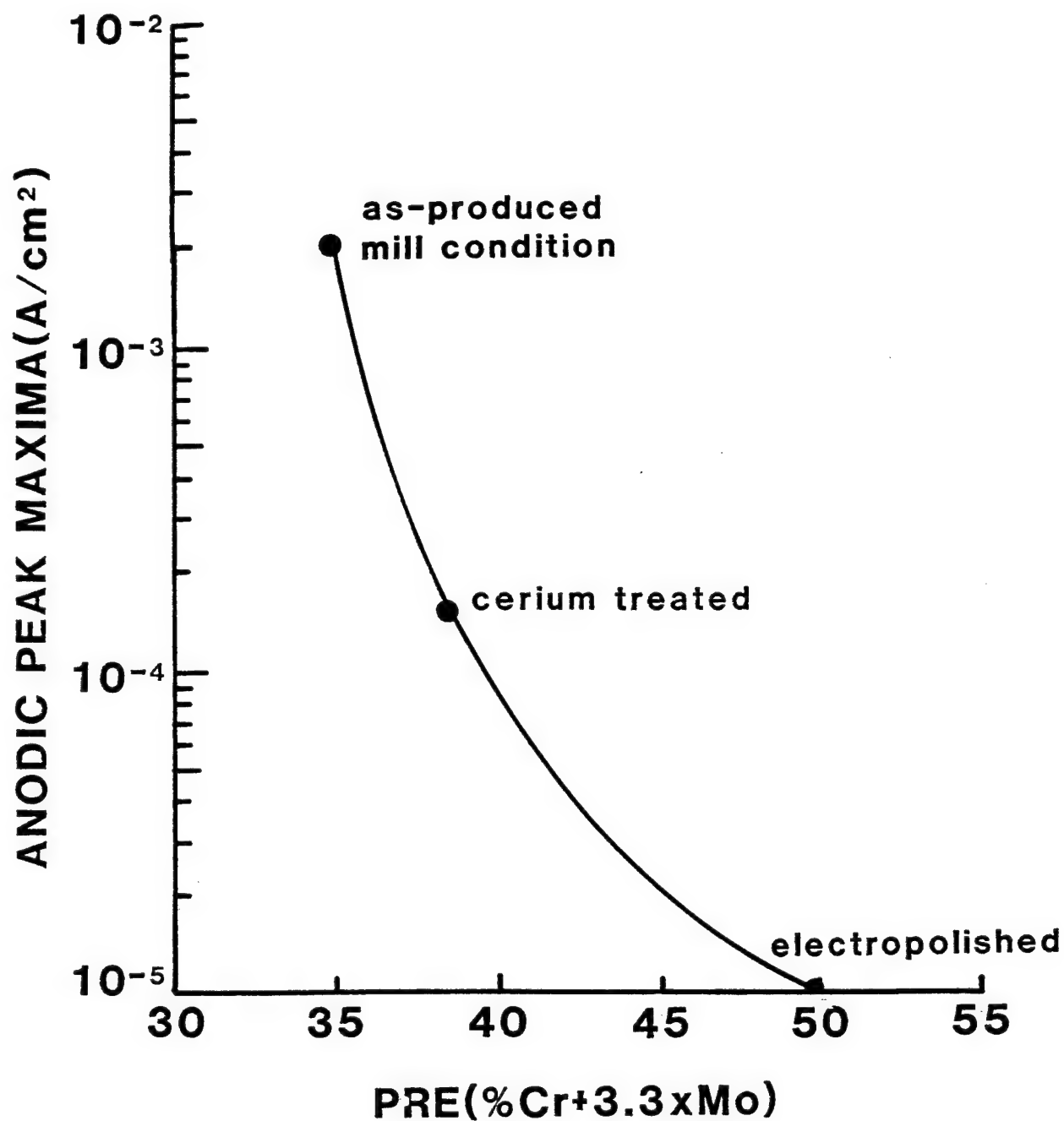
Figure 25.   Relationship between N06625 surface PRE value and anodic current maxima determined in deaerated, simulated crevice solution at pH=0.2.

Process Control Procedures for Electro-Polishing

Used with Permission

Able® Electro-Polishing Company

Introduction

There are a few published procedures on the electro-polishing process. This can be explained by two factors: The electro-polishing market is about 1% of the metal finishing market in general. The relatively small impact of the process has not justified industry or government sponsored standardization. Secondly, most chemical and equipment suppliers use proprietary materials or procedures. The lack of consistent procedures thwart any efforts to standardize between companies.

It is the attempt of this document to publish standard operating procedures for electro-polishing as it is performed by our company. In doing so, it will provide specific standards as they relate to Able® proprietary methods. While these methods may or may not be followed by others, it gives the reader a beginning point in establishing design or quality assurance procedures where electro-polishing is required.

Background of the Process

The first commercial uses for electro-polishing were developed early in the 1950's. Prior to this time, most electro-polishing research was done as a result of successes in electro-plating technology during the 1940's.

Able® Electro-Polishing emerged as the result of developmental work by the parent company, Metco Treating & Development Company. This research involved the application of electro-chemical machining and deburring using a combination of rectified current and an electrolytic bath. While the original intent of the development work was to launch a machining process, the brightening and deburring aspects of electro-polishing were instead pursued. In 1954, Able® Electro-Polishing was formed to provide electro-polishing services to various metalworking companies.

The majority of electro-polishing is done with phosphoric acid-based solutions. Various buffering agents are added to tailor the solution to a specific alloy of metal. Most chemical suppliers offer 5 or more buffered solutions to cover most range of alloys.

Because of the volume of chemicals used, Able mixes its own solutions and uses those solutions on internally designed and manufactured equipment. It is these solutions and equipment that make up the proprietary nature of the Able process.

OVERVIEW OF ABLE ELECTRO-POLISHING PROCEDURES
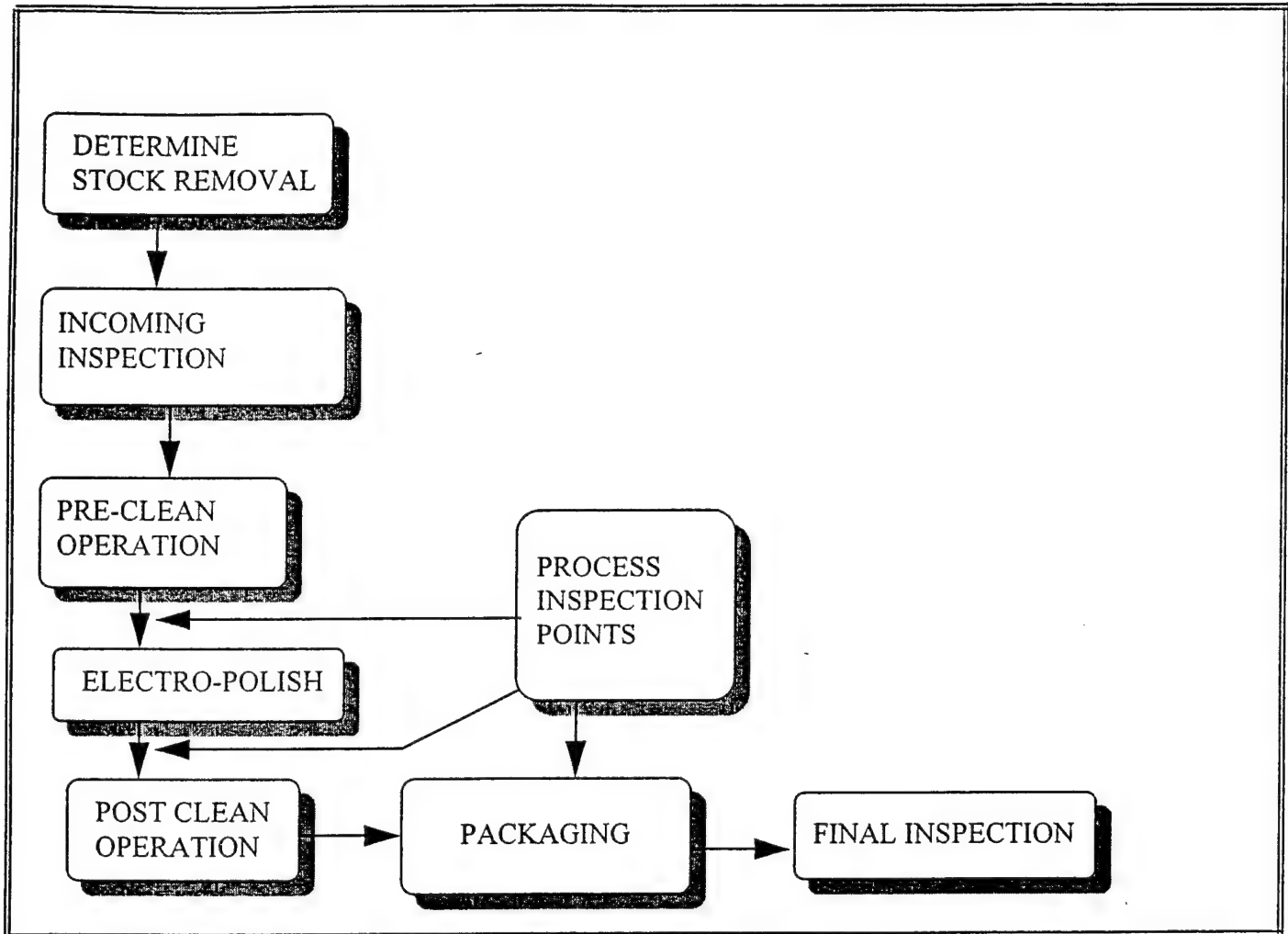
The above flow chart illustrates the process control procedures as performed by Able Electro-Polishing. Detailed procedures follow in this document.

Electro-Polishing Procedures

Determine Stock Removal

Virtually all process control methods require a stock removal standard. Through process experimentation, the desired results are correlated to a specific material removal standard measured per surface. The following are general stock removal information for specific applications:

Deburring:	*.0005 - .0015 removal per surface* *or as required per application*
Micro-Finishing:	*.0001 - .0005 removal per surface* *or as required per application*
Size/Weight Dimension:	*Removal or as required per application*
Bright Passivation:	*.0001 - .001 removal per surface* *or as required per application*
Endurance Finishing:	*.00025 - .0015 removal per surface* *or as required per application*
Decorative:	*Varies to accepted standard sample*

Stock removal standards are established primarily by processing sample parts for customer approval. Those standards are attached to a file copy of the quotation indicating operation conditions and amp/minute readings of the parts. If the quoted, parts become an order. Engineering will then establish process control documentation based on the data generated in the sample run.

Incoming Inspection

Details on inspection procedures and internal document samples are available in the Able® document entitled: "Process Traceability and Quality Control".

The parts are to be inspected prior to any processing. All process control records are pulled and matched to incoming paperwork (packing slips, purchase orders, etc.), and given to the incoming inspector for approval to run. The incoming inspection is performed to determine the following:

- *That the Able process control documents are completely filled out.*
- *That the control documents match customer part numbers and descriptions*
- *That the part is dimensionally in range for processing*
- *That the part is free from visible surface insulators*
- *That the cartons are not damaged or show obvious signs of damage loss to contents*

Should the incoming order not be meeting all above criteria, the paperwork is turned into engineering for a detailed review and/or contact with the customer requesting a variance or return of merchandise.

Pre-Clean

The electro-polishing process is sensitive to the conductivity of the metal surface. Any surface contamination not removed in a proper pre-clean operation may cause surface etching and contamination of polishing baths.

The parts must be free of all surface contaminants including grease, oil and insulators prior to processing. While no one cleaning agent is proper for all surface contaminates, pre-clean procedures are established for a specific part. It is important to note that a change in lubricants or other manufacturing methods prior to electro-polishing may require a change in pre-clean procedures. Able® must be notified of such changes in order to be given the opportunity to alter process procedures.

Most pre-clean operations consist of a singular or multiple use of the following cleaning methods: Degrease, alkaline reverse clean, alcohol scrub. Pre-clean procedures (length of time, temperature of cleaning material, etc.) are to be established for each component.

Electro-Polish

Fixturing: Fixtures are checked for wear. All copper contacts are to be replaced where projected production runs exceed 20 hours on a particular lot. Fixtures are cleaned of all chemicals that may affect electrical contact. The part to be electro-polished is to be fixtured onto the rack for set up purposes. A copper or stainless steel sheet is inserted into the tank and connected as the cathode.

Temperature: Most buffered baths operate in the range of 125 to 150 degrees Fahrenheit. While lower temperatures force longer processing times, higher readings may cause surface etching to occur. An appreciable amount of heat is liberated during the course of treatment. Because of the quality of heat involved, the solution should be agitated during processing to insure a uniform temperature within the processing tank.

Current Density: The amount of amperage drawn during processing must be maintained in the range of 1 to 2 amps per square inch of surface area. Calculations are based on the surface area per part multiplied by the number of parts per process cycle.

Voltage: Rectified current shall range between 5 and 9 volts regardless of solution used.

Process Cycle Time: Time of treatment varies between 1 to 30 minutes per cycle. Cycle time is determined by formulation dependent primarily on temperature and current density. As the temperature increases and/or as current densities increase, cycle times can be reduced.

Post-Clean Operation

To avoid surface staining, all parts must pass immediately from electro-polishing to post-cleaning. While certain alloys or part configurations may require special post-clean procedures (review process control documentation on each part), the majority of parts are cleaned as follows:

1. Spray rinse.
2. Cold water rinse.
3. 10 - 20 % Nitric acid rinse.
4. Cold water rinse.
5. Hot water rinse.
6. ˙Dry (oven or centrifugal method)

On certain assemblies of stainless steel, polishing chemicals become entrapped within welded areas or at gaps between mated metal surfaces. In those cases, the above steps 2 thru 6 are repeated until clean.

Packaging

All parts are to be re-packaged in customer-supplied cartons and packing material except where noted on process control documents. Each shipment is controlled by the Able move ticket and must be labeled by the packer using the standard color-coded label. The label must be filled out containing the following information:

Customer Name
Customer Purchase Order #
Customer Part #
Able Move #
Quantity
Packer #

One color-coded label must be applied to all shipments and˙left visible on a skid of individual cartons.

Final Inspection

Final inspection occurs normally on the shipping dock after an entire shipment is processed and packaged prior to shipment. No shipment is to be released to a carrier until the inspection is complete. Once the Able move ticket is turned in by Packing, it is routed to Final Inspection, together with process control documentation for inspection.

Inspection follows procedures as outlined in the Able document: "Process Traceability and Quality Control". Final inspection reviews the shipment under the following criteria:
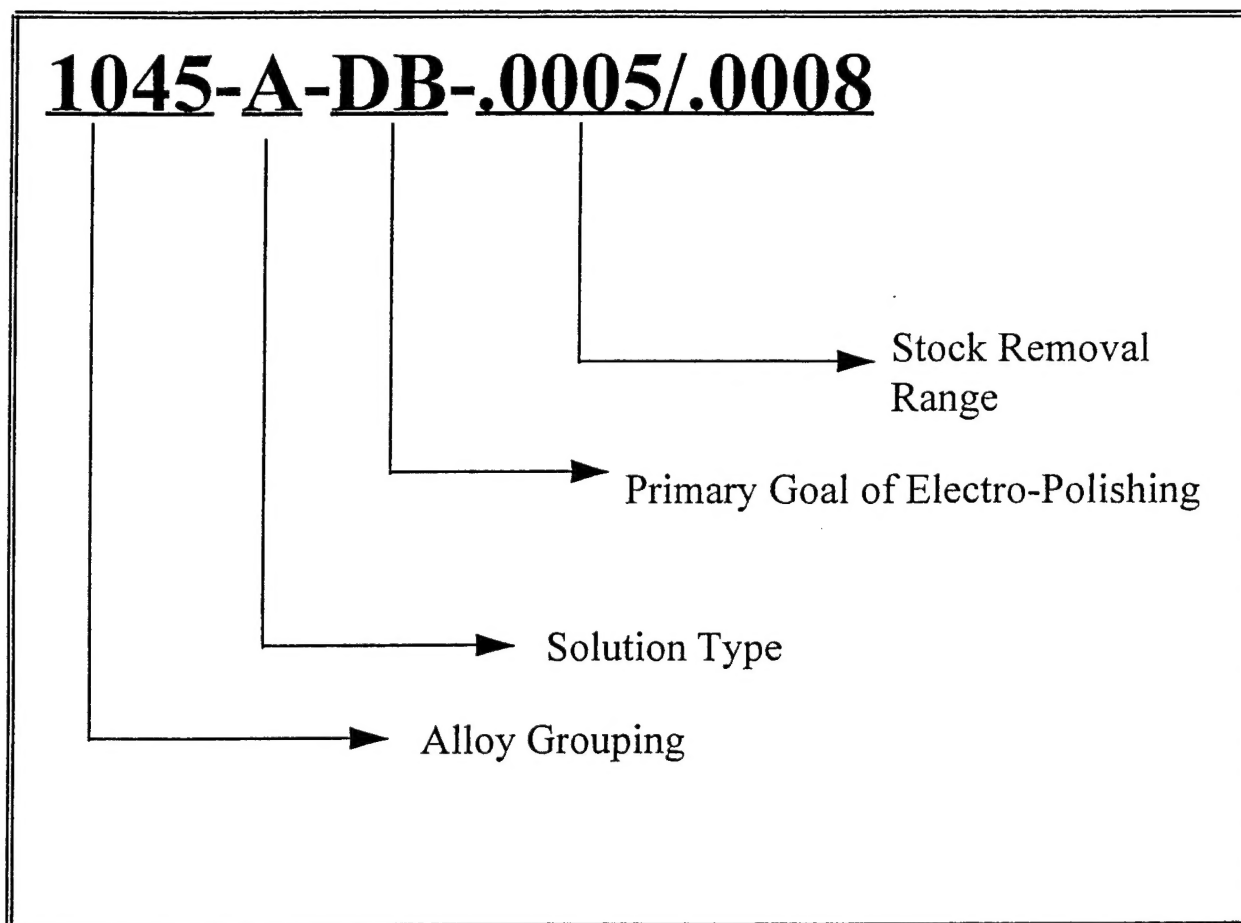
- *That the packing label is present and filled out*
- *That the shipment contains the proper number of cartons*
- *That the shipment is properly banded or attached to skids*

Upon random inspection of individuals cartons:

- *That the parts are packaged per process control documentation*
- *That the parts meet outgoing dimensional tolerances*
- *That the parts are free of stains or chemical residue*

If, upon final inspection of the shipment fails to meet all above criteria, the paperwork is returned to engineering for a detailed review and/or contact with the customer requesting a variance or re-process of parts.

Specification of Process

1045-A-DB-.0005/.0008

Stock Removal Range

Primary Goal of Electro-Polishing

Solution Type

Alloy Grouping

A specification numbering process has been developed. As the above illustration depicts, the numbering format has four distinct parts indicating the alloy of metal, polishing solution, primary process goal and stock removal range.

Alloy Grouping

Alloys are grouped according to their behavior within polishing solutions. For example, alloys in the stainless family behave differently, yet all 300 series alloys and the 202 EZ alloy behave similarly and are grouped as number 1045. The grouped alloys will have the same metal removal rates and generally follow similar post-cleaning procedures.

1040 - 400 series, 17-4 pH stainless steel
1045 - 300 series and 202 EZ stainless steels
1050 - Molybdenum, Hastalloy
1055 - Steel, aluminum (not cast)
1060 - Beryllium copper
1065 - Brass (not cast), Nickel-silver Monel

Solution Type

This reference a specific Able proprietary solution. While Able uses Phosphoric acid as the primary reactive agent, the solution type indicates the proprietary buffering agent that is best used to achieve the desired result (deburring, decorative, etc..) on a specific alloy.

```
A ┐
B │   Solution type
C ├── using
G ┘   Able proprietary
      buffering agents
```

Primary Goal

```
DB - Deburring
CR - Corrosion resistance
MF - Microfinish
DC - Dimensional/weight control
EF - Endurance finishing
DE - Decorative
```

This is the primary purpose for electro-polishing the subject part. By indicating the primary goal, production and quality assurance staff are referred to the specific process control documents for details on achieving an acceptable finish. Many parts use electro-polishing to achieve more than one goal (deburring and decorative, microfinish and corrosion resistance as examples). In those cases, specifying one goal is effective. The process control documentation will provide details as to multiple process goals and procedures.

Stock Removal Range

This indicates the specific stock removal required to achieve the desired goal using the specified solution in the specified alloy range. Virtually all specifications needs a stock removal range. The exception is in cases where processing cycles vary due to varying surface conditions, or where finish tolerances are not critical. Tolerance ranges are generally maintained to $\pm$ .0001".